



EAST HELENA SOURCE APPORTIONMENT STUDY

Particulate Source Apportionment
Analysis Using The Chemical Mass Balance
Receptor Model

VOLUME 1
DRAFT FINAL REPORT

Prepared For
Department of Health and Environmental Sciences
State of Montana

NEA, INC.
8310 S.W. NIMBUS
BEAVERTON, OREGON 97005

September, 1982

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By
James E. Houck
John A. Cooper
Clifton A. Frazier
and
Richard T. DeCesar

NEA, INC.
8310 S.W. Nimbus Avenue
Beaverton, Oregon 97005

September, 1982

Approved by _____
John A. Cooper
President, NEA, INC.

ACKNOWLEDGEMENTS

The completion of this study is due, in large part, to the efforts and cooperation of a number of organizations. These include the State of Montana Department of Health and Environmental Sciences, the U.S. EPA Region VIII, ASARCO, Inc., Ambient Technology, American Chemet Corporation, the Institute of Atmospheric Sciences, South Dakota School of Mines and Technology, and the U.S. Soil Conservation Service. While numerous individuals participated and/or facilitated this study, special thanks go to: David Maughan, Hal Robbins, Ken Alkema, Tom Harris, David Weber, Peter DeSantis, Jim Sieverson, John Nickel, William Porter, Daniel Brimhall, Briant Davis and Monte Bingham.

ABSTRACT

Chemical mass balance source apportionment was utilized to determine the sources of particulate lead and TSP in East Helena, Montana. Ambient and source sample collection was conducted during 1981 and 1982. Mass and elemental analyses for 33 elements were conducted on approximately 700 lo-vol and dichotomous sampler filters collected at twelve sites in and near East Helena. In addition, mass and elemental data were reviewed for approximately 750 hi-vol filters also collected in the East Helena area during that time period. Carbon analysis was conducted on selected ambient samples. The chemical composition for 79 potential particulate sources were compiled and used as the source matrix in the chemical mass balance program. The chemical composition of the 79 sources were obtained by: (1) collection, resuspension and analyses of road and soil dust collected in and near East Helena, (2) collection and analyses of samples from major ASARCO point sources, (3) collection and analyses of samples from process fugitive and minor point sources on the ASARCO and American Chemet plants, (4) collection, resuspension and analyses of samples from industrial storage piles on the ASARCO plant, (5) collection and analyses of samples from area sources and (6) selection of data for general sources from the source file maintained by NEA, Inc. In addition to the CMB source apportionment results, the size distribution of mass and elemental concentrations, bivariate plots and information obtained from previous work were reviewed in reaching the conclusions presented in the report.

Ambient data collected at the Firehall, Muffick, Hadfield, Hastie and Highway sites were selected for detail study. Atmospheric concentrations of lead at these sites can be regularly expected to exceed the arithmetic quarterly mean standard of $1.5 \mu\text{g}/\text{m}^3$. Similarly, atmospheric TSP concentrations at these sites can be expected to approach and often exceed the geometric annual mean standard of $75 \mu\text{g}/\text{m}^3$ unless emissions are reduced. The major sources of TSP at these sites were road dust, fugitive emissions from the handling and storage of ore concentrates and residues, carbonaceous sources (combustion and fugitive), ASARCO's zinc plant and American Chemet's

copper kiln. The major sources of lead in the ambient aerosol were road dust, fugitive emissions from the handling and storage of ore concentrates and residues, blast furnace upsets and ASARCO's zinc plant. Road dust is among the major sources of lead due to its contamination from industrial sources.

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1.0 INTRODUCTION

Atmospheric concentrations of suspended particulate material and lead have exceeded National Air Quality Standards in East Helena, Montana. The State of Montana in response to the Clean Air Act is in the process of developing a lead State Implementation Plan (SIP). Development of a cost-effective SIP control strategy requires an accurate, quantitative understanding of the contributions that each source makes to the atmospheric lead concentration. The study presented here is in response to that requirement.

East Helena is located in the Helena Valley five kilometers east of Helena, the state capital. The Helena Valley is bounded on the north and east by the Big Belt Mountains and on the west and south by the main chain of the Continental Divide. The valley is approximately 40 kilometers in width from north to south and 56 kilometers long east to west. The average height of the surrounding mountains above the valley floor (elevation, 1128 meters) is about 900 meters. The valley can perhaps best be described as broad and flat with limited topographic features. The elevation of East Helena is 1188 meters. The slope of the valley is very gradual in the vicinity of East Helena with the south end of the city limits being less than 15 meters higher than the north end. The boundaries of the lead non-attainment area have not been well defined but appear to be within the city limits of East Helena north of Highway 12 (see Figure 1).

The climate of East Helena can best be described as modified continental. Cold winters with temperatures often reaching well below 0°F (-18°C) and moderate summers with maximum temperatures generally under 90°F (32°C) are typical. The average annual precipitation is 28.9 cm with most precipitation falling between April and July. Snow often remains on the ground for several weeks at a time in the winter. Strong and persistent temperature inversions are common in the Helena Valley. The surrounding mountains shelter the area from winds and at night cold air drains into the valley from the mountain slopes.

Dry-land wheat growing fields and rangeland surround the city of East Helena. A number of different soil types have been documented in and around the city.¹ A railroad (Burlington Northern), a major highway (U.S. Highway 12) and a stream (Prickly Pear Creek) pass through the city. Many unpaved roads, streets and parking lots are in the vicinity. The 1970 population was slightly over 2,000. Two principal industries are located adjacent to and south of the city. These are the ASARCO lead smelting/zinc recovery plant and the American Chemet zinc oxide/copper oxide plant. The ASARCO plant is far larger than the American Chemet plant. Raw and finished materials enter and leave both plants by rail and truck. A limestone quarry is located 4 kilometers to the south. Haul trucks regularly carry limestone from the quarry to the storage area on the ASARCO plant complex. A Kaiser cement plant is located about 5 kilometers south of East Helena. Emissions from its stacks are visible from East Helena. Home heating with wood fuel is common.

The ASARCO lead smelter is a custom lead smelter and it accepts a variety of ores and ore concentrate materials. The plant has a charge capacity of 360,000 tons annually and can yield 60,000 to 100,000 tons of lead bullion per year.² In addition to ores and ore concentrates, other raw materials include coal, coke, limestone and relatively minor amounts of miscellaneous fluxes and additives. Zinc oxide is recovered from the blast furnace slag with a zinc fuming furnace/baghouse process and 25,000 to 40,000 tons of zinc fume are produced annually.² The zinc oxide is shipped by rail to ASARCO's El Paso plant or to the adjacent American Chemet plant. Two other by-products of ASARCO's operation, matte and speiss are shipped by rail to ASARCO's Tacoma plant. One hundred and thirty tons of sulfuric acid is also produced per year at the ASARCO plant from SO₂ generated by the sintering operation.² A lead smelter was first established at the current ASARCO site in 1888. The current East Helena plant averages 340 employees.

The American Chemet Corporation plant is located north of the ASARCO plant complex immediately south of U.S. Highway 12 and west of the bulk of ASARCO's slag storage pile (see Figure 1). The plant was started in 1947 and produces copper oxide and zinc oxide products for feed and fertilizer

supplements, paint pigments and catalysts.² The zinc oxide raw material is obtained primarily from the nearby ASARCO plant. The copper oxide raw materials are obtained from a variety of sources and include such industrial wastes and by-products as: flue dusts from electrolytic furnaces, copper scales, sludge from wire drawing plants and precipitates and solutions of copper salts. There are a number of small stack sources and process fugitive emission sources on the plant.

A major pollution study was conducted in the East Helena area in 1969-70 which was entitled, "Helena Valley, Montana, Area Environmental Pollution Study".⁴ Among the conclusions reached in this study were that airborne heavy metals from the East Helena metal industries settle and accumulate in soil and on vegetation to an extent surpassing levels that are toxic to grazing farm animals and that sub-clinical effects could be occurring in humans due to the heavy metal pollution. The results of previous studies were also discussed in the report. A study conducted by the Montana State Department of Health from October, 1965 to October, 1968 documented the contribution of the smelter complex to ambient arsenic and lead levels when their concentrations dropped during a strike. The study recommended that dust emissions from the smelter complex be reduced, that open burning be prohibited and that street dust be reduced through paving. A study financed by the Montana State Board of Health in December of 1968 reported elevated lead and cadmium levels in garden vegetables and animal tissues from the East Helena area.

Two more recent studies have characterized the emission rates for particulate material and heavy metals from ASARCO point sources⁵ and fugitive sources.⁶ The detailed results of these two studies will not be reproduced here other than noting that each of the three ASARCO point sources (zinc stack, main stack and baghouse stack) were found to emit lead in the tens of kilograms per day range and that measurable lead emissions were detected from each structurally enclosed process on the ASARCO plant. The chemical make-up of the emissions to the extent provided by these studies was consistent with the detailed analyses which were performed in the

study presented here. For example, high cadmium content was found to be contained in emissions from the baghouse stack and from particles originating from blast furnace upsets, a high arsenic content was found in the fugitive emissions from the dropping/reverberatory furnace building and a moderate arsenic concentration was found in particles emitted from the main stack. The only important discrepancy in these two reports and the conclusions reached in the study reported here is that the dropping/reverberatory furnace building was concluded to have a high emission factor whereas the CMB modelling conducted in this study did not identify it as a major source impacting East Helena. It is possible that the modifications made in the dropping/reverberatory furnace building after the earlier emission measurements were made is responsible (see Appendix B, reference 7).

A dispersion model utilizing 1978 meteorological data and emission rates from references 5 and 6 was conducted for East Helena, Montana.⁷ The study substantially underpredicted the ambient lead levels that should be observed in the city but did conclude that the major point sources (i.e., the tall stacks) would have an insignificant impact on lead concentration at the near-plant ambient monitors, that the process fugitive emissions would show a high lead impact and that vehicular exhaust would show a small but measurable impact. It was concluded that the ambient lead levels were substantially underpredicted because fugitive dust (industrial and geological) and sporadic emission episodes such as blast furnace upsets were not taken into account.

A direct receptor model approach was used in this study to quantitatively apportion lead and TSP source contributions at East Helena ambient monitoring sites. This method apportions source contributions on the basis of physical and chemical features of particles collected at a receptor (sampler) and is independent of often unknown and highly variable meteorology and emission factors. This approach has been applied to numerous airsheds over the past decade in the form of chemical mass balance, factor and regression analysis.⁸⁻¹¹ Chemical mass balance (CMB) methods provide the highest level of quantification when source chemical fingerprints are

available, and it was the basic model used in this study. The chemical fingerprints for 79 sources were compiled, most were from the direct measurement of East Helena sources, several fingerprints for ubiquitous sources (e.g., vehicular exhaust) were obtained from the source files maintained by NEA, Inc. Ambient samples were collected from twelve sites during 1981 and 1982. Nearly seven hundred ambient samples as well as the source samples were analyzed for mass and 33 elements. The CMB modelling performed with this extensive data base coupled with ancillary information such as was obtainable from bivariate plots and mass and elemental size distributions permitted detailed quantitative source apportionment to be conducted on the East Helena ambient aerosols.

This report is divided into three volumes. Volume I contains the textual part of the report including the tabulation of key data sets and results. Volumes II and III contain the appendices. The appendices are comprised of: (1) standard operating procedures and documentation of techniques used for sampling and analysis, (2) the source fingerprints for all three size fractions of sources used in the CMB model and (3) the CMB printout results.

2.0 PROGRAM METHODOLOGY

The program methodology contains four key elements which are necessary to accomplish source apportionment. These are: (1) ambient sample collection, (2) source sample collection and characterization, (3) chemical and mass analyses of ambient and source samples and (4) chemical mass balance modelling.

2.1 Ambient Sampling

Three types of samplers were used for ambient sampling. These were high volume TSP (Total Suspended Particles), low volume TSP and dichotomous samplers. Filters collected with high volume samplers were analyzed for mass and elemental concentrations by the State of Montana. Filters collected with low volume TSP and dichotomous samplers were analyzed for mass and elemental concentrations by NEA, Inc.

Dichotomous samplers collect two size categories of particles. One filter collects particles of less than 2.5 microns in aerodynamic diameter, the other filter collects particles with aerodynamic diameters between 2.5 and 15 microns. Particles of less than 2.5 microns and particles of less than 15 microns are size categories related to health considerations and are often referred to as respirable and inhalable particles, respectively.

Both low volume and high volume samplers were employed to collect TSP samples. High volume samplers using glass fiber filters is the technique on which U.S. EPA mass and lead standards have been based. Low volume samplers collect samples on analytically clean teflon filters (as do dichotomous samplers) which permit accurate multi-element analysis which is needed for CMB (chemical mass balance) modelling. Low volume TSP samplers do not collect particles greater than approximately 30 microns due to their inlet design. Consequently, low volume TSP samplers will produce mass concentration ($\mu\text{g}/\text{m}^3$) values slightly less than high volume TSP samplers operating at the same site over the same time period.

It should be noted that particles of greater than 30 microns have a short residence time in air and are generally considered to be from fugitive sources. The data reduction and interpretation presented in this report are largely based on sample sets when dichotomous, low volume and high volume samples were co-collected (same time period and same site) to permit differences in sample collection mass and chemistry to be understood and to provide insight into the origin of the ambient aerosol.

Figure 1 illustrates the principal sampling sites. Samples were collected from January, 1981 through April, 1982. Nearly 700 valid dichotomous and low volume teflon filters were collected and analyzed for mass and elemental concentrations during that time period (Tables 1 and 2). The routine sampling program was conducted entirely in calendar year 1981 (Tables 3-6).

The most extensive sampling program was conducted during the fourth quarter of 1981 (Table 6). Sampling during the fourth quarter was conducted by the contractor, Ambient Technology. Sampling during the first three quarters of 1981 was conducted by the State of Montana and ASARCO. The few samples collected during 1982 were for illustrative purposes (i.e., comparison between low volume and high volume samplers, comparison between elemental and mineralogical data and examination of data from a new site). The State of Montana collected the samples obtained in 1982. In addition to the teflon filters, several low volume samples on quartz filters were obtained for carbon analysis and several high volume glass fiber filter samples were also obtained for carbon analysis. Mass and elemental data (to the extent available) were reviewed in this report for approximately 750 high volume samples collected in 1981 in addition to the 700 teflon low volume and dichotomous filters.

NEA, Inc. provided all low volume and dichotomous filters, special field sampling and shipping boxes for the filters and the low volume samplers. Standard Operating Procedures (SOP's) for sampler operation and filter handling and shipping have been prepared and are included in Appendix A.



Figure 1 AMBIENT SAMPLE COLLECTION SITES

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Table 1

NUMBER OF VALID SAMPLES ON WHICH ANALYSES WERE PERFORMED
 AT EACH SAMPLING SITE,
 EAST HELENA, MONTANA (1981)

SITE	DICHOT. SAMPLES	LO-VOL SAMPLES
Canal	44 (88 filters)	48
Dartman	0	26
Firehall	29 (58 filters)	28
Hadfield	38 (76 filters)	41
Hastie	26 (52 filters)	27
Highway	0	23
Microwave	9 (18 filters)	0
Muffick	7 (14 filters)	6
Padbury	0	45
South	29 (58 filters)	28
Vollmer	0	42
TOTAL	³⁶⁴ 182 (362 filters)	³¹⁴ 308

Table 2

NUMBER OF VALID SAMPLES ON WHICH ANALYSES WERE PERFORMED
AT EACH SAMPLING SITE
EAST HELENA, MONTANA (1982)

SITE	DICHOT. SAMPLES	LO-VOL SAMPLES
Canal	0	1
Dartman	0	2
Hadfield	1 (2 filters)	3*
Hastie	1 (2 filters)	4*
Highway	0	1
South	0	2
Reserv.	4 (8 filters)	3
TOTAL	6 (12 filters)	15 ¹⁶

*Includes one hi-vol 8" x 10" teflon filter.

Table 3

VALID SAMPLE SCHEDULE
QUARTER 1

MONTH	CANAL				FIREHALL					HASTIE	VOLLMER	
	Fine	Coarse	L.V.	H.V.	Fine	Coarse	L.V.	S.W. H.V.	N.E. H.V.	H.V.	L.V.	H.V.
JAN												
4				X						X		
10				X					X	X	HT027	X
16										X	HT032	X
21				X	HD033	HD034	HT031					
22				X				X	X	X		X
28	HD036	HD035	HT035	X				X	X	X	HT013	X
FEB												
3	HD013	HD014	HT014	X	HD025	HD026	HT036	X	X	X	HT015	X
5				X			HT018	X		X	HT017	X
9	HD019	HD020	HT020	X	HD022	HD023	HT019	X		X	HT021	X
12	HD016	HD015	HT023	X	HD030	HD029		X	X	X		X
15			HT004	X	HD002	HD001	HT003	X	X	X	HT002	X
21	HD007	HD008	HT006	X			HT005	X	X	X	HT007	X
24	HD012	HD011	HT009	X	HD006	HD005	HT008	X	X	X		
27			HT012	X			HT011	X	X			
MAR												
2	HD050	HD049	HT038	X	HD048	HD047	HT037	X	X	X		
5	HD056	HD055	HT040		HD054	HD053	HT039	X	X			
8	HD052	HD051	HT042	X	HD058	HD057	HT041	X	X	X		
11	HD059	HD060	HT049	X	HD061	HD062	HT043	X	X			
14	HD066	HD065	HT052	X	HD064	HD063	HT050	X	X	X		
17	HD070	HD069	HT053		HD068	HD067		X		X		
20	HD074	HD073	HT055	X	HD072	HD071	HT060	X	X	X	HT054	X
24	HD077	HD078	HT057	X	HD076	HD075	HT056	X	X	X	HT058	X
26			HT062	X	HD080	HD079	HT059	X	X	X		X
29					HD086	HD083	HT063	X	X	X		

An x in the hi-vol (H.V.) column indicates a valid sample was collected.

The codes in the fine and coarse dichotomous filter columns and in the lo-vol (L.V.) columns are the valid sample I.D. numbers.

0030491

Table 4

VALID SAMPLE SCHEDULE
QUARTER 2

MONTH	CANAL				FIREHALL					MICROWAVE			HASTIE	VOLLMER		MUFFICK					PADBURY		SOUTH
	Fine	Coarse	L.V.	H.V.	Fine	Coarse	L.V.	S.W. H.V.	N.E. H.V.	Fine	Coarse	H.V.	H.V.	L.V.	H.V.	Fine	Coarse	L.V.	W. H.V.	E. H.V.	L.V.	H.V.	H.V.
APR																							
1	HD085	HD084	HT065	X	HD088	HD087	HT066	X	X				X	HT064	X								
3				X				X	X				X		X								
4	HD090	HD089	HT068		HD092	HD091	HT067							HT069									
7			HT072	X	HD094	HD093	HT070	X	X				X		X								
10	HD098	HD097	HT074	X	HD096	HD095	HT073	X	X				X	HT075	X								
13	HD102	HD101	HT077	X	HD100	HD099		X	X				X	HT078	X								
16	HD106	HD105	HT079		HD104	HD103		X	X				X	HT080	X								
19	HD110	HD109	HT086	X	HD108	HD107	HT087	X	X				X	HT085	X								
22	HD115	HD114	HT089	X	HD112	HD111	HT088	X	X				X	HT090	X								
25			HT092	X	HD116	HD113	HT084	X	X			X	X	HT093	X								
28	HD118	HD117	HT095	X	HD120	HD119	HT094	X	X			X	X	HT083	X								
MAY																							
1	HD124	HD123	HT097	X	HD122	HD121		X	X			X	X		X								
4			HT100	X			HT099	X	X			X	X		X								
7	HD134	HD133	HT103	X	HD132	HD131	HT102	X	X			X	X	HT104	X								
10	HD128	HD127	HT081	X	HD130	HD129	HT105	X	X			X	X		X								
13	HD126	HD125	HT106	X								X	X		X								
16				X								X	X	HT108	X								
19			HT109	X								X	X	HT110	X								
22			HT111	X								X	X		X								X
25			HT113	X								X	X	HT112	X								X
28	HD136	HD137	HT114	X								X	X	HT115	X								X
31				X								X	X	HT117	X	HD142	HD143		X	X	HT118	X	X
JUN																							
3	HD146	HD147		X								X	X	HT120	X	HD148	HD149	HT121	X	X	HT122	X	X
6				X								X	X		X	HD150	HD151	HT119	X	X	HT124	X	X
9	HD158	HD159		X								X	X		X	HD156	HD157	HT125	X	X	HT126	X	X
12	HD168	HD167		X								X	X		X	HD166	HD165	HT127	X	X	HT128	X	X
15	HD170	HD169		X								X	X		X	HD162	HD163	HT129	X	X	HT130	X	X
18	HD176	HD175		X								X	X		X	HD174	HD173	HT131	X	X		X	X
21	HD188	HD187		X								X	X		X						HT134	X	X
24				X								X	X		X							X	X
27	HD194	HD193		X								X	X		X							X	X
30				X								X	X		X							X	X

An x in the hi-vol (H.V.) column indicates a valid sample was collected.

The codes in the fine and coarse dichotomous filter columns and in the lo-vol (L.V.) columns are the valid sample I.D. numbers.

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Table 5

VALID SAMPLE SCHEDULE
QUARTER 3

MONTH	CANAL				MICROWAVE			HASTIE	VOLIMER		PADBURY		SOUTH	HIGHWAY		HADFIELD					DARTMAN
	Fine	Coarse	L.V.	H.V.	Fine	Coarse	H.V.	H.V.	L.V.	H.V.	L.V.	H.V.	H.V.	W. H.V.	E. H.V.	Fine	Coarse	L.V.	W. H.V.	E. H.V.	H.V.
JUL																					
3	HD184	HD183		X			X	X		X		X	X								
6				X			X	X		X		X	X								
9				X			X	X		X		X	X								
12				X			X	X		X		X	X								
15				X			X	X		X		X	X								
18				X			X	X		X			X								
21				X			X	X				X	X								
24				X			X	X		X		X	X								
27				X			X	X		X		X	X								
30			HT136	X			X	X	HT137	X		X	X	X	X						
AUG																					
2			HT138	X			X	X	HT139	X		X	X	X	X						
5			HT140	X			X	X	HT141	X		X	X	X	X						
8			HT142	X			X	X	HT143	X		X	X	X	X						
11				X				X	HT144	X	HT145	X	X								
14				X				X	HT147	X			X						X	X	
17				X			X	X	HT148	X		X	X						X	X	
20			HT149	X			X	X	HT150	X		X	X						X	X	
23	HD206	HD205	HT151	X	HD208	HD207	X	X	HT152	X		X	X			HD204	HD203	HT153	X	X	
26	HD244	HD243	HT156	X			X	X	HT157	X	HT158	X	X			HD210	HD209	HT155	X	X	
29	HD234	HD233	HT160	X			X	X		X	HT162	X	X					HT159	X	X	X
SEP																					
1	HD240	HD239		X			X	X	HT165	X	HT166	X	X			HD238	HD237	HT163	X	X	X
4			HT168	X			X		HT169	X	HT170	X	X					HT167	X	X	X
7				X			X			X		X	X					HT171	X	X	X
10	HD264	HD259	HT174	X			X			X	HT176	X	X			HD252	HD251	HT173	X	X	X
13	HD254	HD253	HT178				X	X	HT179	X	HT180	X	X			HD260	HD261	HT177	X	X	X
16	HD250	HD265		X	HD258	HD249	X	X	HT181	X	HT182	X	X			HD262	HD263		X	X	X
19				X			X	X	HT197	X	HT198	X	X					HT194	X	X	X
22	HD280	HD279	HT200	X			X		HT201	X	HT202	X	X			HD278	HD277	HT199	X	X	X
25	HD268	HD267		X	HD270	HD269	X	X		X	HT206	X	X			HD266	HD257	HT203	X	X	
28																					X

An x in the hi-vol (H.V.) column indicates a valid sample was collected.

The codes in the fine and coarse dichotomous filter columns and in the lo-vol (L.V.) columns are the valid sample I.D. numbers.

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Table 6

VALID SAMPLE SCHEDULE
QUARTER 4

MONTH	CANAL	DARTMAN		HADFIELD					HASTIE				HIGHWAY	MICRO WAVE	PADBURY		SOUTH				VOLLMER
	H.V.	L.V.	H.V.	FINE	COARSE	L.V.	W. H.V.	E. H.V.	FINE	COARSE	L.V.	H.V.	L.V.	H.V.	L.V.	H.V.	FINE	COARSE	L.V.	H.V.	H.V.
OCT																					
1	X			HD290	HD289	HT207	X	X			HT211	X		X	HT210	X	HD294	HD293	HT208	X	X
4			X	HD304	HD305	HT213	X	X	HD292	HD291	HT216	X			HT214	X	HD302	HD301	HT215	X	
7	X		X	HD314	HD313	HT218	X	X	HD316	HD315	HT219	X		X	HT217	X	HD318	HD317	HT220	X	X
10		HT224	X	HD308	HD307	HT222	X	X	HD310	HD309	HT223	X	HT225		HT221	X	HD312	HD311	HT226	X	
13	X	HT230	X	HD322	HD321	HT228	X	X	HD306	HD303	HT229	X	HT232	X			HD320	HD319	HT231	X	X
16		HT236	X	HD324	HD323	HT234	X	X	HD326	HD325	HT235	X	HT233		HT227	X	HD328	HD327	HT237	X	
19		HT241	X	HD330	HD329	HT239	X	X			HT240	X	HT242		HT238					X	
26		HT244	X	HD352	HD351	HT249		X	HD354	HD353	HT243	X	HT245		HT248	X	HD360	HD359	HT246	X	X
29	X		X	HD362	HD361	HT250		X	HD356	HD355		X		X	HT247	X	HD358	HD357	HT270	X	X
NOV																					
1		HT274	X	HD364	HD363	HT279	X	X	HD370	HD369	HT273	X	HT276		HT278	X	HD366	HD365	HT275	X	
4	X	HT281	X	HD372	HD371	HT280	X	X					HT282	X	HT277		HD368	HD367	HT283	X	X
6		HT350	X	HD446	HD445	HT349	X	X	HD448	HD447	HT348	X	HT284		HT346	X	HD450	HD449	HT347	X	
9	X	HT352	X	HD454	HD453	HT353	X	X	HD452	HD451	HT345	X	HT354	X	HT351	X	HD456	HD455	HT355	X	X
12		HT358	X	HD458	HD457	HT359	X	X	HD462	HD461	HT356	X	HT361		HT357	X	HD460	HD459	HT362	X	
15	X	HT253	X	HD344	HD343	HT260	X	X	HD374	HD373	HT258	X	HT254	X	HT255	X	HD346	HD345	HT259	X	X
18		HT262	X	HD338	HD337	HT252	X	X	HD340	HD339	HT263	X	HT265		HT267	X	HD342	HD341	HT261	X	
21	X	HT251	X	HD336	HD335	HT266	X	X	HD332	HD331	HT264	X	HT257	X	HT268	X	HD334	HD333	HT256	X	
24		HT364	X	HD350	HD349	HT369	X	X	HD348	HD347	HT363	X	HT366		HT368	X	HD464	HD463	HT365	X	
27	X	HT371	X	HD466	HD465	HT370	X	X	HD468	HD467	HT372	X		X	HT367	X	HD470	HD469	HT374	X	
30		HT307	X	HD472	HD471	HT317	X	X	HD474	HD473	HT306	X	HT360		HT316	X	HD418	HD417	HT308	X	
DEC																					
3	X	HT313	X	HD420	HD419	HT311	X	X	HD422	HD421	HT312	X		X	HT310	X	HD424	HD423	HT314	X	X
6		HT378	X	HD476	HD475	HT376	X	X	HD478	HD477	HT375	X	HT380		HT377	X	HD480	HD479	HT379	X	
9	X	HT384	X	HD482	HD481	HT382	X	X					HT386	X	HT381	X	HD484	HD483	HT388	X	X
12		HT387	X	HD486	HD485	HT392	X	X	HD488	HD487	HT383	X	HT389				HD490	HD489		X	
15	X	HT323	X	HD510	HD509	HT321	X	X	HD512	HD511	HT322	X	HT325	X	HT391	X	HD514	HD513	HT324	X	X
18		HT326	X	HD504	HD503	HT328	X	X	HD506	HD505	HT327	X	HT335		HT329	X	HD508	HD507	HT336	X	
21	X	HT333	X	HD502	HD501	HT331	X	X	HD430	HD429	HT332		HT337	X	HT330	X	HD426	HD425	HT334	X	X
24		HT341	X	HD428	HD427	HT339	X	X	HD436	HD435	HT340		HT394		HT338	X	HD438	HD437	HT393	X	
27	X	HT398	X	HD440	HD439	HT396	X	X	HD518	HD517	HT397	X	HT399	X	HT395	X	HD520	HD519	HT400	X	X
30		HT413	X	HD522	HD521	HT411	X	X	HD442	HD441	HT412	X				X	HD516	HD515	HT414	X	

An x in the hi-vol (H.V.) column indicates a valid sample was collected.

The codes in the fine and coarse dichotomous filter columns and in the lo-vol (L.V.) column s are the valid sample I.D. numbers.

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Ambient Technology has prepared a number of documents describing the ambient samplers and sampling network (including the results of audits and calibrations) which is included as Appendix J.

2.2 Source Sampling and Characterization

To obtain the detailed chemical composition of aerosol sources which was necessary for chemical mass balance modelling, an extensive source sampling program was conducted. Figure 2 schematically illustrates three categories of particulate sources and the method used to collect representative samples of the aerosols they produce. The three types of aerosol sources are: (1) point sources (stacks), (2) process fugitive sources and (3) passive fugitive sources.

Table 7 lists the point sources and process fugitive sources sampled at East Helena. Structures that enclosed process areas were sampled with standard dichotomous and low volume samplers located near roof vents. On the ASARCO plant complex, the D & L building (sinter building), the New Deal building (ore proportioning building), the zinc plant (zinc furnace building), the dross building (dross kettle/reverberatory-furnace building) and the zinc fume baghouse building were sampled in that fashion, as well as American Chemet's zinc kiln room. Particles produced by blast furnace upsets and slag pouring were sampled by positioning equipment in an area where their episodic emission "plume" would impact it heavily. The samplers were started when a slag pour commenced or when the first sign of a furnace upset was noted. The samplers were shut off when the plume from the respective events no longer visually impacted the samplers. A single filter was left on the samplers so that a cumulative sample was collected from representative sampling of a number of short term emission plumes. A cumulative sample was desirable to integrate emission variability and collect a relatively large sample mass for chemical analysis. Both dichotomous and low volume samplers were used to sample blast furnace upsets. Only a low volume sampler was used to collect the slag pouring aerosol due to the difficulty of positioning equipment near the high temperature molten slag.

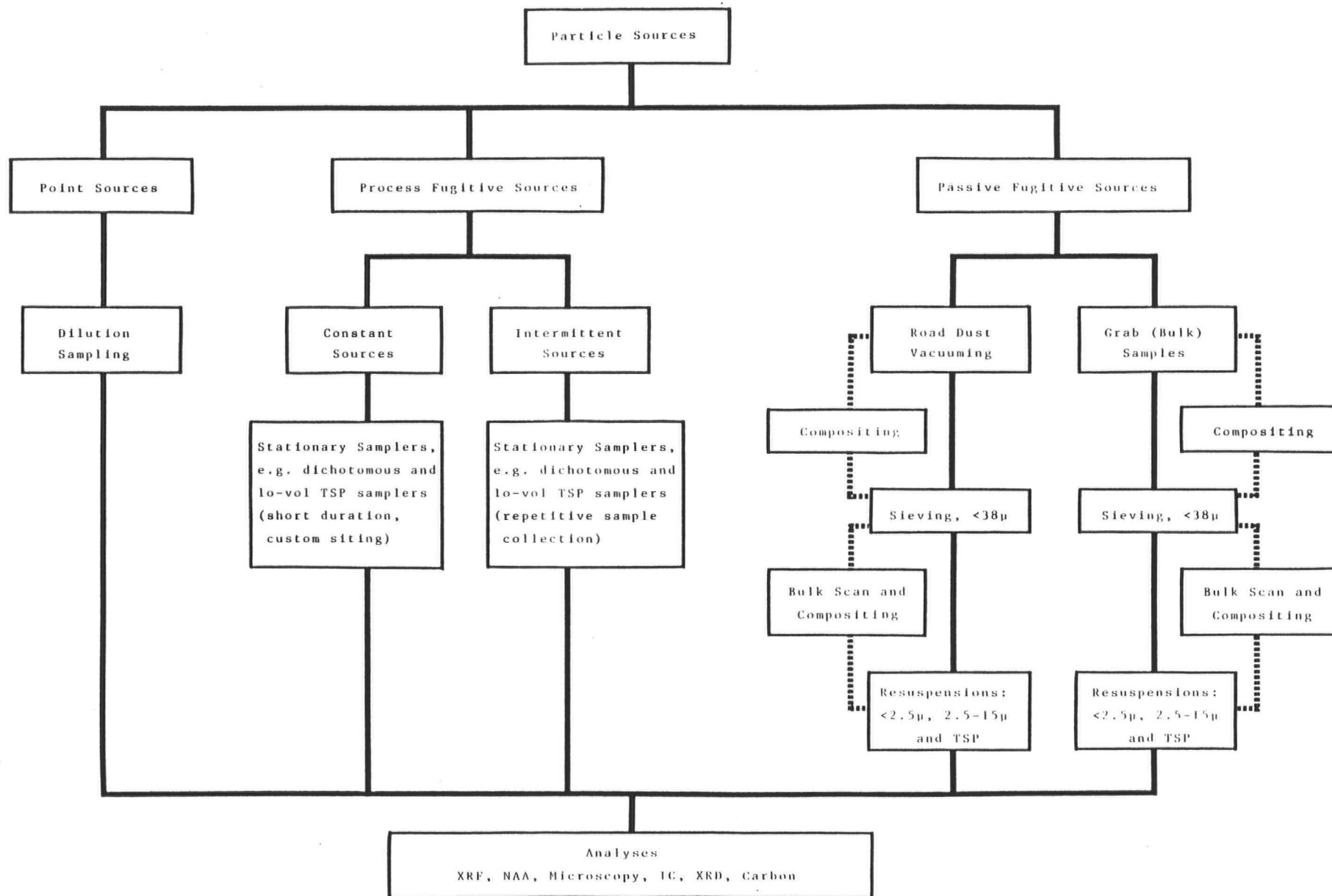


Figure 2 Schematic of Aerosol Source Sampling

Table 7

Process Fugitive, Stack and Miscellaneous Sources

<u>Source Code</u>	<u>Description</u>
DLBLD	D & L Building
NDBLD	New Deal Building
ZNBLD	Zinc Plant
DRBLD	Dross Building
ZNBGB	Zinc Baghouse
BLFUP	Blast Furnace Upset
MSSTK	Main Sinter Stack
ZNSTK	Zinc Stack
BGSTK	Baghouse Stack
SLPOR	Slag Pour
ZNKLR	Zinc Kiln Room
ZNKLD	Zinc Kiln Discharge
CUKST	Copper Kiln Stack
CUINC	Copper Incineration
DIESL	Diesel Exhaust
SECO	$(\text{NH}_4)_2\text{SO}_4$ - Secondary Sulfate
WSTOV	Helena Wood Stove
TRANS	Vehicular Exhaust
RDOIL	Residual Oil Combustion

The three major ASARCO stacks were sampled with a dilution/cooling system (Figure 3). The three stacks are (1) the zinc fuming stack, (2) the main (sinter) stack and (3) the baghouse (blast furnace) stack. A complete description of dilution source sampling for chemical mass balance source apportionment is presented in Appendix B. The fundamental purpose of dilution sampling is to collect stack particles in the form they are in after mixing and cooling with ambient air which occurs when they are emitted from the stack environment. The dilution sampling system isokinetically withdraws a sample of stack gas, mixes it with filtered ambient air at a dilution ratio of between 20:1 to 100:1, and collects a size categorized sample ($<2.5\mu$ and $>2.5\mu$) onto teflon filter media. The temperature at the point of sample collection is generally only several degrees above ambient and the filter media used for sample collection is identical to that used for ambient field sampling which facilitates comparisons between the chemistry of stack and ambient aerosols. By cooling and diluting stack aerosols, the chemistry and size distribution obtained is closer to that which actually impacts ambient sites due to condensation, vaporization, agglomeration and secondary chemical reactions which would not occur if a sample were collected directly inside the stack.

In addition to the process fugitive and stack sources sampled by standard techniques, several other sources were sampled and are listed in Table 7. American Chemet's copper kiln stack was sampled by holding a high volume stack sampler fitted with an 8" X 10" teflon filter over the stack and by holding scalping cyclones followed by a back-up teflon filter also over the stack. This was determined to be the most appropriate sampling strategy since there were no available stack sampling ports and the stack plume was at low temperature at the point of sample collection. Similarly, American Chemet's zinc kiln discharge vent was sampled by positioning a low volume sampler in the horizontally directed discharge flow. A wood smoke sample was collected in Helena due to the proximity of residential wood combustion stacks to several of the ambient sampling sites. Wood smoke samples were collected with low volume and dichotomous samplers which were held in a wood smoke plume (Table 8). A laboratory simulation of

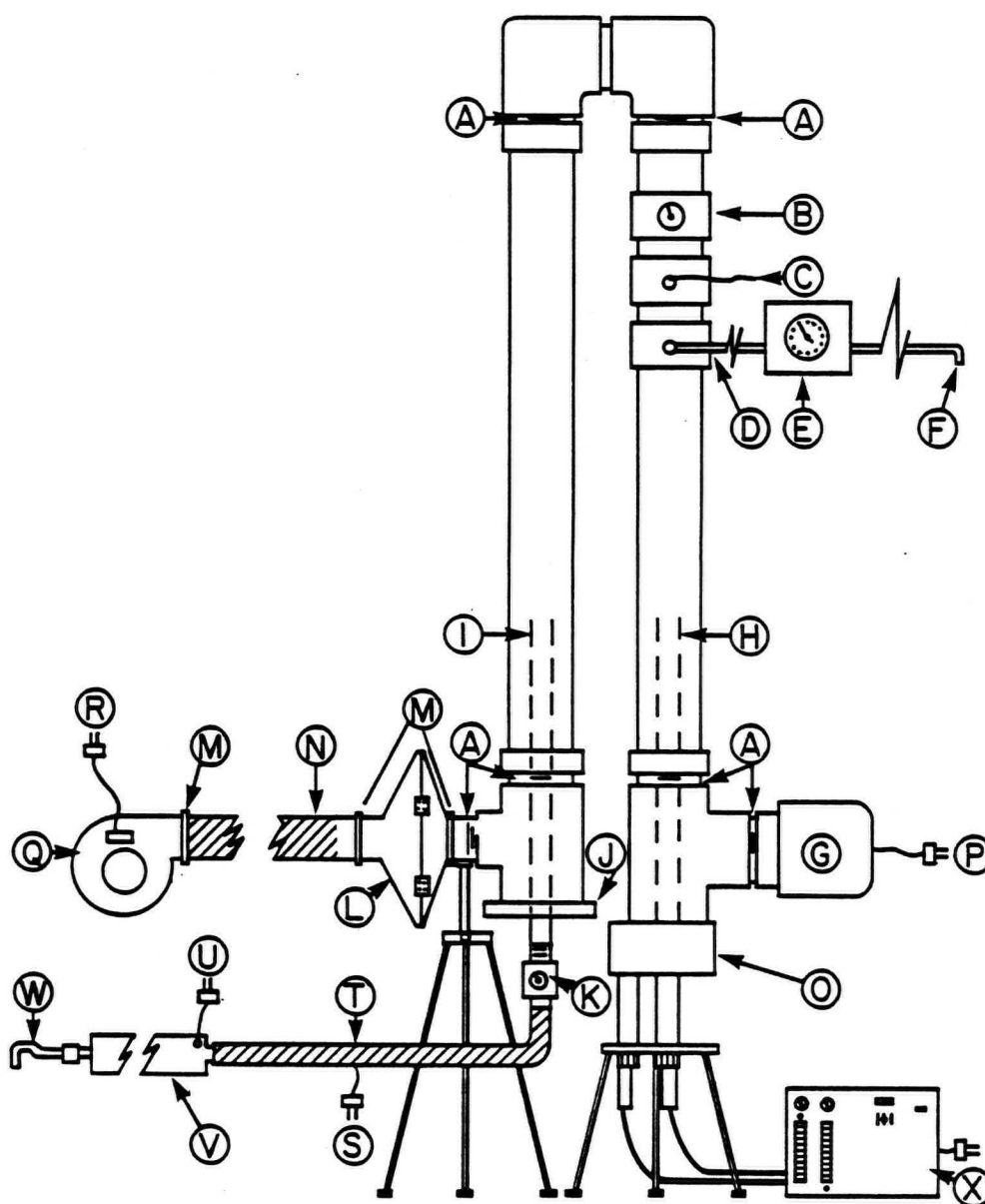


Figure 3. Dilution Source Sampler

(Not drawn to scale.) Height is approximately 2 meters, and unit is constructed with 10.2 cm (4 inch) diameter pipe. Design features include: (A) Threaded connectors for disassembly and transport, (B) thermometer, (C) gas velocity sensor to thermal anemometer, (D) static pressure sensor, (E) Magnehelic gauge, (F) total pressure sensor for in-stack measurements, (G) high volume vacuum motor, (H) interchangeable (0.64 to 2.54 cm I.D.) dichotomous inlet pipe, (I) stack gas inlet pipe, (J) stainless steel and asbestos end assembly, (K) threaded union with thermometer, (L) hinged 20 cm x 25 cm (8 inch x 10 inch) filter holder, (M) quick disconnect fittings, (N) flexible hose, (O) dichotomous sampler head, (P) power cord from high volume vacuum meter to a variable transformer, (Q) high volume blower, (R) power cord to a variable transformer, (S) power cord to heat tape, (T) insulated stainless steel teflon tubing, (U) power cord to heat tape, (V) 1.5 meter stainless steel stack probe, (W) button-hook sampling nozzle, and (X) dichotomous sampler control unit.

Table 8

Wood Stove Samples Collected January 19, 1982

David Maughan

Run	Start	Flow End	Lapsed Time	Filters	Comments
(#1)	T-16.7 1/min C-1.67	4.0 1/min 0.60	7 min 5 sec	C-HD523 F-HD524	Fire condition-two logs exterior burned off but still uncracked through center. Unburned wood on ends. Ashes cleaned out about 6 hours prior to test. Pine wood (both dry and green). Low fire about 1/4 way through burn process.
(NEA Tare wts HD 523 - 92.09 mg HD 524 - 93.14 mg)					
(#2)	T-16.7 C-1.67	16.6 1.65	15 min.	C-FRED6 F-FRED5	Fire conditions - as above, but less visible smoke. Fire temperature increased toward end of test period. Continuation of run #1 burn.
(#3)	T-16.7 C-1.67	4.3 0.3	15 min	C-HD525 F-HD526	Fire conditions - new, dry pine logs; substantial smoke; some large visible soot particles suspended in smoke beginning of burn.
(#4)	T-16.7 C-1.67	16.5 1.64	30 min.	C-FRED3 F-FRED4	Fire conditions - burning hot and fast during first 10 minutes then damped down. Dry pine used during burn. Continuation of run #3.

February 3, 1982

(#5)			8.5 min.	FRED1 47 mm quartz	Fire start-up with one medium-sized split, dry pine piece of wood. Smoke gray to black.
(#6)			15.0 min	FRED2 47 mm quartz	Just after fire start-up, mostly dry pine but with some dry fir. Hot fire which generated very little smoke, consequently stove air inlet was shut-down by about 75%. Fire burned at about 33% of heating capacity. Minimal whitish smoke visible from chimney.
(#7)			10 min.	HT415 47 mm TFE	Wood mixture as above. Hot fire but few flames - red hot coals. Few visible emissions from chimney during test. Stove air reduced by about 75% to generate medium smoke.

Stove Description - (Fisher Papa Bear) air tight wood stove with a 23-foot brick over clay-flue-lined chimney. All were in excellent condition.

Outside temperature during tests was about 5-10°F. A Sierra dichotomous sampler was modified for the tests by placing a seven-foot pipe between the bead and the particle separation unit. Typically this pipe is about 10 inches long. The sampler head, pipe, and separator were cleaned prior to the tests. The pump unit worked properly.

particles produced by American Chemet's copper incineration stack was conducted by the State of Montana and the particles produced were collected with a low volume sampler (Table 9). A large diesel exhaust sample was collected by State of Montana personnel with a high volume sampler. The material collected with the high volume sampler was removed, resuspended in the laboratory into $<2.5\mu$, $2.5-15\mu$ and TSP size categories. Additionally, several source fingerprints were taken from NEA's Source Library and are listed in Table 7. Those were (1) secondary sulfate $(\text{NH}_4)_2\text{SO}_4$, (2) vehicular exhaust and (3) residual oil combustion. A total of nineteen point source, process fugitive source and relevant miscellaneous source fingerprints were compiled for the East Helena Study.

The resuspension of dust by vehicular traffic has been shown to be a major source of coarse particles ($>2.5\mu$) and a minor source of respirable particles ($<2.5\mu$) in numerous studies. Road dust is particularly important in and around industrial complexes due to the increased vehicular traffic associated with industry and track-out of commercial materials. The characteristic chemistry and morphology of resuspended road dust originating from commercial materials is typically quite distinct as compared to urban or rural road dust. The sampling strategy for road dust collection entailed collection of samples from haul roads, urban streets, highways and rural roads.

A modified hi-vol sampler was used to collect road dust samples. Using the hi vol "vacuum" sampler, samples were collected from paved roads, unpaved roads, coarse gravel roads and from railroads. Once the road dust samples were collected, the samples were sieved and resuspended in the laboratory onto dichotomous and lo-vol TSP samplers. A number of the samples were composited to reduce the total number of samples on which detailed analysis had to be performed. Appendix A lists the detailed procedures for road dust sample collection and the subsequent laboratory procedures for resuspension.

Windblown dust from material storage piles, waste piles, exposed soil surfaces, etc. is an important source of particles particularly in the coarse size fraction. Grab sampling followed by laboratory sieving and resuspension was used to characterize the ambient particles originating from these sources.

Table 9

EAST HELENA CHEMET INCINERATION SAMPLES
January 7, 1982

David Maughan

- Test 1 HT 320 for 9 min 40 sec. using NEA 10-vol added about 6 grams of American CHEMET red copper material (Sample 21 Grab sample D, collected 11/12/81) from railroad tracks west of CHEMET. Material was placed in a stainless steel beaker, heated with a lab-flamed-burner to red hot temperature. The SS-beaker was supported in an inverted gallon-size clear glass pyrex beaker. A NEA 10-vol filter was supported adjacent to the top of the beaker, but also within the inverted glass bowl. The whole apparatus evolved considerable whitish smoke. The tests were performed in a Department of Health laboratory hood.
- Test 2 HT-318 Void. Sample flow was increased at the 10-vol pump and the filter was positioned within the smoke plume--but the filter holder melted.
- Test 3 HT-319 for 4 minutes but with decreased flow. We used about 15 grams CHEMET copper scale material. (Sample already sent to NEA about January 20, 1982.)

The collection of representative grab samples from each friable industrial storage pile, dusty unpaved roads where the road dust sampler could not be used, and from exposed soil surfaces such as agricultural fields produced many more samples than could be analyzed within the scope of this project. To reduce the total number of individual samples, bulk and soil (and road dust) samples were composited. Three approaches to compositing were taken. For the slag pile with a very large surface area, a transect sampling plan was developed and a large number of samples were collected, composited to form integrated samples representative of large areas of the slag pile, then sieved and resuspended. For soil and road dust samples collected from various locations which could not be assumed a priori to be similar in composition, the samples were first sieved to less than 38 μ , then a semi-quantitative XRF scan was conducted on the bulk samples. Based on the similarities or dissimilarities detected by the XRF scan, the samples were composited before resuspension and before detailed analyses were conducted. For the ore concentrates and residues samples, only those materials which were routinely stored in large quantities were resuspended and analyzed. Samples from different piles of ore concentrates or residues from the same source (as identified by ASARCO records) were composited to produce a more representative sample. An overall composite fingerprint was also formed for ore concentrates and residues by mathematically averaging the elemental concentration data determined for all the ore concentrate and residue samples analyzed. This overall composite fingerprint is identified by the source code ORCOM in Appendix D.

Nineteen composite road dust and soil samples were formed and analyzed (Table 10). These were formed from nineteen individual soil samples and twenty-one road dust samples collected in the East Helena area (Tables 11 & 12). Figures 4 and 5 illustrate the soil and road dust collection sites.

Twenty-six miscellaneous bulk samples were collected, resuspended and analyzed (Table 13). These bulk samples were primarily industrial materials and by-products stored in the East Helena area. One winter road sanding/salting mixture was also included among the samples. Four of the miscellaneous bulk samples were slag composites. A description of the slag

Table 10

COMPOSITE SOIL, ROAD DUST AND RAILROAD SAMPLES

SAMPLE I.D.	CONSTITUENT SAMPLES	DESCRIPTION	RATIONALE	RESUSPENSION I.D.		
				FINE	COARSE	LO-VOL
A	Soil 1	Padbury Site soil	Background soil	RS420	RS421	RL045
B	Soil 2	Microwave Site soil	Very high Ca	RS422	RS423	RL046
C	Soils 3, 4, 5, 6, and 15	Vollmer Site soil & soil collected near water tank west of ASARCO.	High Ca Low Pb, Cu & Zn	RS450	RS451	RL058
D	Soils 7, 8, 9, 999 (16), 18 & 19	Canal Site soil above Prickley Pear Creek flood plain near Dartman Site	Slightly lower Ca than Sample C; Slightly higher Pb, Cu & Zn than Sample C	RS452	RS453	RL059
E	Soil 10	Soil from bank immediately south of Hadfield Site	Intermediate levels of Ca, Pb, Cu & Zn	RS424	RS425	RL047
F	Soils 11, 12, 13 & 14 Road Dusts 13 & 18	Soil from around Firehall Site, from Prickley Pear flood plain and from dirt road to houses west of ASARCO	Higher Ca than samples C & D, low Cu, Zn appx. same as sample D, Pb same as Sample C	RS454	RS455	RL060
G	Soil 1000 (17)	Turn around area next to paved roadway, American Chemt, RR & dirt road west of ASARCO	Highest soil Cu, Zn & Pb; high Ca	RS426	RS427	RL048
H	Road Dust 1	Interstate Hwy, 200 meters south of Padbury	Impact of Hwy on background site	RS428	RS429	RL049

Table 10

COMPOSITE SOIL, ROAD DUST AND RAILROAD SAMPLES (cont.)

SAMPLE I.D.	CONSTITUENT SAMPLES	DESCRIPTION	RATIONALE	RESUSPENSION I.D.		
				FINE	COARSE	LO-VOL
I	Road Dust 2	Gravel road leading to Padbury Site	Impact of gravel road on background site	RS432	RS433	RL050
J	Road Dusts 3 & 11	Mont. Ave. leading to ASARCO housing and Hwy 287, 200 meters south of RR tracks	Impact on Hastie & Canal Sites, intermediate Cu & Zn, high Ca & Pb	RS456	RS457	RL061
K	Road Dust 4 & 5	Hwy 12	Impact on Hwy on Hadfield, Highway & Firehall Sites	RS458	RS459	RL062
L	Road Dusts 6, 7, 8 & 9	City streets adjacent to Firehall and Hadfield Sites	Intermediate Pb & Ca, high Zn & Cu	RS460	RS461	RL063
M	Road Dust 10	Probable impact of fugitive dust from limerock haul trucks	Very high Ca	RS434	RS435	RL051
N	Road Dust 12		Hwy impact on Canal Site	RS436	RS437	RL052
O	Road Dust 15	Probable impact of traffic to ASARCO plant	Impact on Hadfield, Firehall & Highway Sites	RS438	RS439	RL053
P	Road Dust 17	City street	Impact on Hastie Site	RS440	RS442	RL054
Q	Road Dust 20		Hwy impact on Hastie Site	RS443	RS444	RL055

Table 10

COMPOSITE SOIL, ROAD DUST AND RAILROAD SAMPLES (concluded)

SAMPLE I.D.	CONSTITUENT SAMPLES	DESCRIPTION	RATIONALE	RESUSPENSION		
				FINE	COARSE	LO-VOL
R	Road Dust 21	Gravel Road	Impact on South Site	RS445	RS446	RL056
S	Railroad 1		RR impact on Hadfield, Highway & Firehall Sites	RS447	RS449	RL057

Road Dust Samples 14 and 16 were not composited as no sample stations were near these collection sites; there is no Road Dust Sample 19.

See additional tables for specific date and location of each individual soil, road dust and railroad sample.

Comments on chemistry in rationale column based on analysis of bulk samples ($< 38 \mu$)

Table 11
East Helena
Soil Samples

<u>Sample No.</u>	<u>Date</u>	<u>Location and Comments</u>
1	9/15/81	15 meters east of Padbury Station, musselshell loam (high in lime).
2	9/15/81	Sampled several locations 10 to 15 meters from Microwave Station, fill material similar to Crago loam.
3	9/15/81	Plowed field 10 to 15 meters from Vollmer Station, Crago loam.
4	9/15/81	Sandy wash bottom and dirt road, 100 meters west of Vollmer Station, recent alluvium, sandy loam, low in lime.
5	9/15/81	Plowed field 100 meters west of Vollmer Station and 100 meters north of Sample #4, down hill from sampler and generally upwind. Sappington loam, less lime than Sample #3.
6	9/15/81	Wheat field (mostly bare ground) 200 meters west of Vollmer Station (very little lime).
7	9/15/81	30-35 meters S-SW of Canal Station, Nippt very cobbly loam, low in lime.
8	9/15/81	100 meters W-SW of Canal Station, Attewan loam.
9	9/15/81	5 meters east of Canal Sampling Station, very resuspendable material on dirt road to Sampling Station, Nippt cobbly loam.
10	9/15/81	Sample taken on bank 7 meters south of Hadfield Station, approximately 3 meters lower in elevation than sampling platform. Local fill material.
11	9/15/81	Dirt parking lot 25 meters north of Firehall Station.

Table 11 (cont.)

East Helena
Soil Samples

<u>Sample No.</u>	<u>Date</u>	<u>Location and Comments</u>
12	9/15/81	Low point between Pacific Street and Highway 12, 20 meters south of Firehall Station, probably transported and deposited by flood of May 22, 1981, silt-loam alluvium.
13	9/15/81	Prickly Pear Creek Bed, below high water mark, approximately 0.5 kilometers north of East Helena city limits, very cobbly sand and loamy sand, Dartman Ranch.
14	9/15/81	Integrated sample collected on recent flood plain (May 22 flood) between Prickly Pear Creek and Dartman Ranch, sample integrated approximately 200 meters of distance, all recent alluvium, same distance from East Helena as Sample #13.
15	9/15/81	Sample collected from dirt road near water tank 0.8 kilometers west of ASARCO plant. Road was along SW edge of plowed field, musselshell loam, high in lime, approximately 35 meters higher in elevation than East Helena.
999 (16)	9/16/81	Sample collected on Highway 287 right-of-way approximately .5 kilometers east of plant and 200 meters south of railroad.
1000 (17)	9/16/81	Sample collected in turn-around area next to paved roadway, American Chemet, railroad and dirt road to houses west of ASARCO.
18	9/24/81	Transect SE of Dartman monitors.
19	9/24/81	NW corner of Kleffner wheat field 300 yards south of Canal monitors.

Table 12

East Helena

Road Dust and Railroad Samples

<u>Sample No.</u>	<u>Date</u>	<u>Location and Comments</u>
RD1	9/16/81	Interstate 15, 200 meters south of the Padbury Station, east lane headed north.
RD2	9/16/81	Gravel road leading to Padbury residence, single lane 4 meters wide, approximately 35 meters N.W. of Padbury Station.
RD3	9/16/81	Montana Avenue leading to ASARCO housing east of plant, on railroad right-of-way.
RD4	9/16/81	Highway 12, directly across from American Chemet on the south and Cleveland Avenue on the north. Approximately 75 meters south of the Hadfield sampling station. Four lane highway, east bound lane only, no curb, center of road was concrete.
RD5	9/16/81	Same as sample 4 except west bound lane, curb on north side.
RD6	9/16/81	Cleveland Street, 15 meters east of Hadfield Station, no curbs.
RD7	9/16/81	Main Street, 20 meters north of Hadfield Station, curb on north side of street, none on south side.
RD8	9/16/81	Corner of Pacific and Cleveland Streets, 1 block (~50 meters) south of the Hadfield Station, curb on north side, none on south side.
RD9	9/16/81	Corner of Morton Street and Pacific Street directly in front of Firehall Station. Curb on east side of Morton Street.
RD10	9/16/81	Junction of Highway 287 and ASARCO haul road, paved road.
RD11	9/16/81	Highway 287, 200 meters south of railroad.
RD12	9/16/81	Highway 12, east end of East Helena, approximately 40 meters north of Canal Station.
RD13	9/16/81	Dirt road to houses west of ASARCO, south of railroad.
RD14	9/16/81	Junction of gravel road and paved road, 75 meters west of baghouse stack, sample from gravel road.
RD15	9/16/81	Highway just west of ASARCO and Chemet, just south of railroad track.
RD16	9/24/81	Gravel road about 200 feet SSW of Sinter stack near ASARCO entrance into cooling towers.

Table 12 (cont.)

East Helena
Road Dust and Railroad Samples

<u>Sample No.</u>	<u>Date</u>	<u>Location and Comments</u>
RD17	9/24/81	Paved street 75 feet south of Hastie monitors, no curbs.
RD18	9/24/81	Driveway dust - dirt/gravel, Dartman residence, about 100 feet SSW of sampler.
*		
RD20	9/24/81	Four-lane paved highway south of Hastie monitors. Sample includes median area and both west and east lanes. North edge does have curb, but not south.
RD21	9/24/81	Abandoned gravel road just north of south monitor and at Kleffner property boundary. Part of the sample included pasture area below the monitors.
RR1	9/16/81	Burlington Northern Railroad adjacent and north of American Chemet, sample collected with road dust sampler.

* No Road Dust Sample 19.

RD - Road Dust

RR - Railroad

Table 13

MISCELLANEOUS BULK SAMPLES

SAMPLE I.D.	DATE OF COLLECTION	DESCRIPTION AND/OR LOCATION	RESUSPENSION I.D.			COMMENTS
			FINE	COARSE	LO-VOL	
I-1	11-81	Clean-up pile C from lower storage area.	RS356	RS369	RL009	
I-2	11-81	Dross skims from six-high bins.	RS358	RS359	RL010	
I-3	11-81	Sinter from stock pile belt near blast furnace.	RS360	RS361	RL011	
I-4	11-81	Sulfur flux from six-high bins.	RS362	RS363	RL015	
I-5	11-81	Lime rock from lake shore storage area.	RS364	RS365	RL013	
I-7	11-81	Blast furnace baghouse dust.	RS366	RS368	RL014	
I-8	11-81	Acid plant hot cottrell & baghouse dust.	RS370	RS373	RL016	
I-9	11-81	Soda from six-high bins.	RS374	RS375	RL017	
I-10	11-81	Zinc oxide from ASARCO zinc oxide baghouse.	RS378	RS379	RL019	
I-11	11-81	American Chemet copper kiln discharge.	RS376	RS377	RL018	
I-12	11-81	American Chemet zinc fume (marketed product).	RS380	RS381	RL020	
I-14	11-81	Granulated coke from six-high bins.	RS382	RS383	RL021	
I-15	11-81	Black, beaded granular material (perhaps coke) collected from near thaw house.	RS384	RS387	RL022	

Table 13

MISCELLANEOUS BULK SAMPLES (continued)

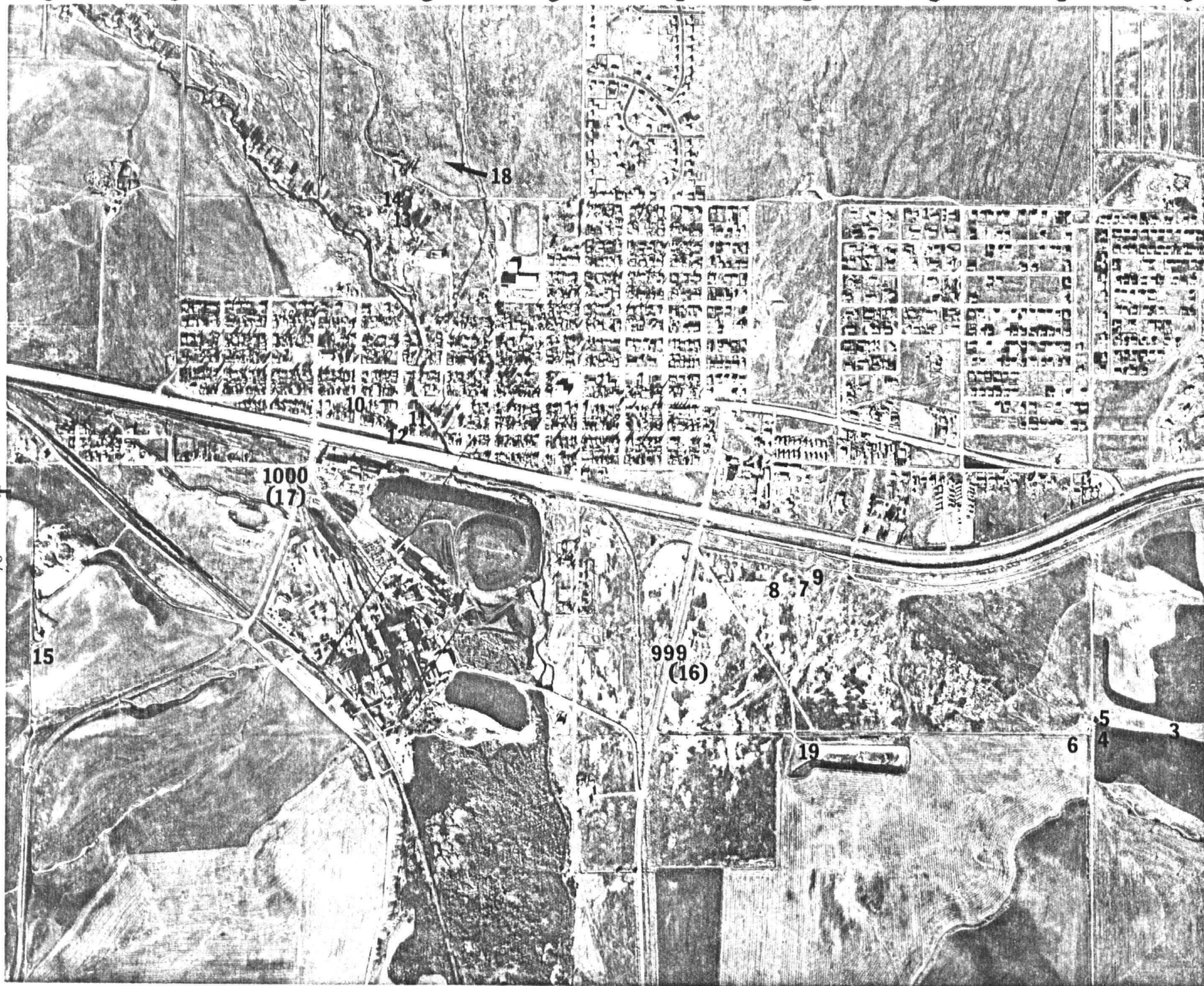
SAMPLE I.D.	DATE OF COLLECTION	DESCRIPTION AND/OR LOCATION	RESUSPENSION I.D.			COMMENTS
			FINE	COARSE	LO-VOL	
I-16	11-81	Granular coal or coke collected from pile NE of thaw house.	RS388	RS389	RL023	
I-17	11-81	Coal from pile west of Pile 58.	RS390	RS391	RL024	
I-18	11-81	Coal from pile north of Pile 58.	RS392	RS393	RL025	
I-19	11-81	Coal from Pile 58 in coal storage area on west end of plant near American Chemet.	RS394	RS416	RL026	
I-20	12-81	Sand and salt used on icy roads. Collected by David Maughan.	RS412	RS413	RL035	
II-2 (Grab Sample J)	9-81	Red colored material collected on RR right-of-way west of American Chemet.	RS404	RS405	RL031	
II-3 (Grab Sample Q; Grab Sample 24)	9-81	Black material collected on RR right-of-way west of American Chemet.	RS406	RS407	RL032	
III-1 (Grab Sample A)	9-81	Coke collected from RR right-of-way west of ASARCO.	-	-	RL044	Sample ground. Resuspended on Lo-vol only.

Table 13

MISCELLANEOUS BULK SAMPLES (concluded)

SAMPLE I.D.	DATE COLLECTION	DESCRIPTION AND/OR LOCATION	RESUSPENSION I.D.			COMMENTS
			FINE	COARSE	LO-VOL	
III-3	11-81	Speiss (fresh material) from pile storage area near dross building.	-	-	RL-040	Sample ground. Resuspended on Lo-vol only.
IV-1	11-81	Slag Sample Composite W.* Formed from 12 samples collected on west "leg" of slag pile.	RS396	RS417	RL042	
IV-2	11-81	Slag Sample Composite C.* Formed from 6 samples collected on center mound of slag pile.	RS398	RS399	RL028	
IV-3	11-81	Slag Sample Composite S.* Formed from 4 samples collected on south "leg" of slag pile.	RS400	RS401	RL029	
IV-4	11-81	Slag Sample Composite M.* Formed from 6 samples collected in slag mining area.	RS402	RS419	RL030	

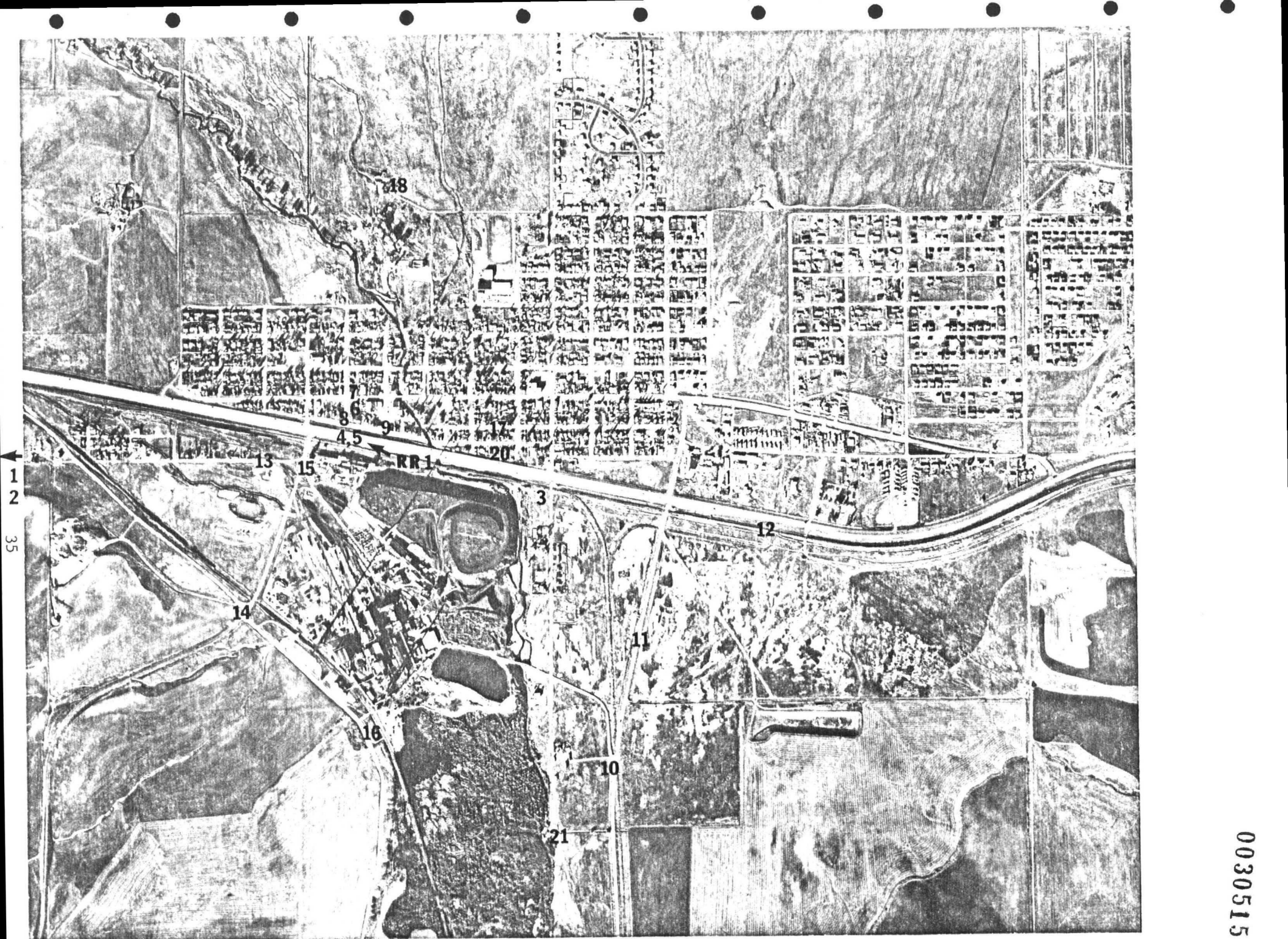
*See Table for description of slag sample composites.



↓ 2

Figure 4 Soil Sample Collection Sites

0030514



0030515

Figure 5 Road Dust Collection Sites

composite is given in Table 14. The fourteen ore concentrate and residue samples are described in Table 15. Appendix A lists the procedures for bulk and soil sample collection and the subsequent procedures for laboratory resuspension.

2.3 Chemical and Mass Analysis

Thin film energy dispersive x-ray fluorescence spectrometry (XRF) was performed on all valid ambient and source samples collected with the dichotomous, lo-vol and dilution samplers. The XRF analysis was accomplished with an Ortec TEFA III model 6110-40 analyzer. Three excitation conditions were used for each sample (Table 16). XRF calibration was accomplished with three types of standards: (1) thin film vapor deposited standards made by Micromatter, Inc., (2) multielement solution deposited standards prepared by Columbia Scientific Industries and (3) particle standards also prepared by Columbia Scientific Industries. The standards were verified by theoretical plots of instrument response versus atomic weight.

For each XRF analysis run of ten samples, a quality control standard was analyzed. Measured concentrations of this standard, which contains several key elements, were compared with actual concentrations. If the deviation was more than $\pm 2\%$ for any of the elements, all samples in that run were re-analyzed. Several elements, including K, Ca, Fe, As, Br and Pb, were measured under more than one of the three excitation conditions used. Results of these elements were compared for each of the excitation conditions under which they were measured. If agreement was not within error bars, the sample was re-analyzed. For each XRF analysis run of ten samples, a blank was also run.

To further verify the accuracy and precision of data obtained by thin film x-ray fluorescence spectrometry, NEA, Inc. participated in an EPA sponsored interlaboratory comparison of polymer film standards prior to this study. Seven other laboratories participated in the intercomparison and in addition to energy dispersive XRF, other analytical techniques were used.

Table 14

COMPOSITE SLAG SAMPLES

Composite W

West 1/3 of slag pile (zinc stack plateau and face of plateau)

1. Slag from north side of slag pile across from Main Street
2. Slag from north side of pile across from American Chemet, Inc.
3. Slag from north side of pile across from Firehall
4. Slag from north side of road up slag pile
5. Slag from near base of zinc stack (2 samples)
6. Slag from 100 meters east of zinc stack
7. Slag from 200 meters northeast of zinc stack
8. Slag from in-between zinc stack and west side of slag pile
9. Slag from west side of slag pile
10. Slag sample taken at west end of intermediate plateau - sample 999 (2 samples)

Composite C

Central 1/3 of slag pile (top of slag pile and along face of top pile)

1. Sample B collected with road dust sampler
2. Slag sample from northeast face of slag pile
3. Slag sample from bank above plant manager's home just below trolley car track.
4. Sample C collected with road dust sampler
5. Slag sample taken along trolley car track; north face of slag pile
6. Sample A collected with road dust sampler

Composite S

South 1/3 of slag pile (scrap iron storage area and area east of zinc plant)

1. Slag sample from scrap iron dump area
2. Slag from near trolley car track toward zinc plant
3. Slag from pile near trolley car track
4. Slag from old slag dumping station

Composite M

Slag mining area (6 samples)

Table 15

ORE CONCENTRATES AND RESIDUE COMPOSITES
(SAMPLES COLLECTED NOVEMBER 1981)

COMPOSITE I.D.	CONSTITUENT SAMPLES	RESUSPENSION I.D.			COMMENTS
		FINE	COARSE	LO-VOL	
O-A	Pile 427 - Glover dross Pile 782 - Glover	RS462	RS463	RL064	Sample formed solid mass when dried. Ground and resuspended onto lo-vol only.
O-B	Pile 592 - Omaha Dust			RL093	
O-C	Pile 713 - Bunker Residue	RS464	RS467	RL065	
O-D	Pile 794 - SSPy/TGS Pile 852 - TGS Pile 868 - TGS	RS468	RS469	RL066	
O-E	Pile 811 - Mixed Residue	RS470	RS471	RL067	
O-F	Pile 847 - Rumley	RS472	RS473	RL068	
O-G	Pile 848 - Keno	RS474	RS475	RL069	
O-H	Pile 522 - Castro Pile 524 - Castro Pile 703 - Castro Pile 705 - Castro Pile 706 - Castro Pile 850 - Castro Pile 864 - Castro Pile 1057 - Castro Pile 1060 - Castro Pile 1062 - Castro Pile 1110 - Castro	RS476	RS477	RL070	
O-I	Pile 812 - Buick Pile 855 - Buick	RS478	RS479	RL072	

Table 15

ORE CONCENTRATES AND RESIDUE COMPOSITES
(SAMPLES COLLECTED NOVEMBER 1981)

COMPOSITE I.D.	CONSTITUENT SAMPLES	RESUSPENSION I.D.			COMMENTS
		FINE	COARSE	LO-VOL	
O-J	Pile 753 - Galena Pile 784 - Galena Pile 853 - Galena	RS480	RS482	RL073	
O-K	Pile 756 - Tacoma dust Pile 791 - Tacoma dust Pile 813 - Tacoma dust Pile 857 - Tacoma dust Pile 872 - Tacoma	RS483	RS484	RL075	
O-L	Pile 798 - MT Isa Pile 799 - MT Isa Pile 800 - MT Isa Pile 801 - MT Isa Pile 802 - MT Isa	RS485	RS486	RL074	
O-M	Pile 858 - Quiruvilea Pile 859 - Quiruvilea	RS487	RS489	RL076	
O-N	Pile 863 - Alianza Pile 865 - Alianza	RS491	RS492	RL077	

Table 16

X-Ray Fluorescence Operating Conditions

Parameter	Condition 1	Condition 2	Condition 3
Anode Element	Mo	Mo	W
Tube Voltage (KV)	50	15	35
Tube Current (μ amp)	200	200	200
Filter Element	Mo	none	Cu
Analysis (live) time (sec)	50-400	20-400	30-400
Energy Range (KeV)	0-40	0-10	0-20
Elements Measured	Fe, Ni, Cu, Zn, Ga, As, Se, Br, Rb, Sr, Y, Zr, Pd, Ag, Cd, In, Sn, Sb, Ba, La, Hg, Pb	Al, Si, P, K, Ca, Fe	S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, As, Br, Pb

These included instrumental neutron activation analysis, optical spectroscopy and wavelength dispersive XRF. Results of the comparison study are presented in Appendix K.

In addition to XRF analyses, selected source samples were analyzed by instrumental neutron activation (NAA) to expand the elements measured and to confirm the values obtained by XRF. This was done due to the unusual chemical composition of some of the source samples. Since XRF is a non-destructive technique, the same samples on which XRF analysis was performed were used in the INAA analysis. Two irradiation/cooling/counting conditions were used. The two sets of conditions are commonly referred to as "shorts" and "intermediate-longs".

The neutron activation analyses were conducted at the Reed College Reactor facility. Samples were irradiated at 95% full power in the Triga Mark I 250 KW reactor. The neutron flux was 5×10^{12} n/cm²-sec. A pneumatic transfer system was used for sample handling. Copper flux monitors permitted normalization of flux for each sample to standards. Standards included a NBS urban particulate standard reference material (SRM #1648), an IAEA soil standard (#5), an USGS soil reference material (BRC-1), an ARHCO basalt standard (#1) and gravimetric standards prepared at NEA's laboratory. For the short analyses, the irradiation time was 5 minutes, the cooling time was 10 minutes and the counting time (live) was 200 seconds. For the intermediate-long analyses, the irradiation time was 8 hours, the cooling time was 10 days and the counting time was 2 hours. The samples were counted with a 17% Ortec HpGe gamma-ray spectrometer interfaced with a Norland IT-5400 multichannel ancilyzer (4096). The elements Dy, Ti, Br, Mn, Mg, In, Na, V, Cl, Al and Ca were measured in the short analyses. The elements Ce, Lu, Th, Cr, Yb, Ba, Cd, As, Br, Ag, Sc, Rb, Fe, Zn, Co, La and Sb were measured by the intermediate-long analyses. A number of these elements were routinely at concentration levels below detection limits.

Mass determinations were performed on all valid samples using a Cahn Model 27 Electrobalance. The weight of the filters prior to sample collection and after sample collection was determined with the same instrument.

Filters were weighed in sets of 20 or less. Calibration of the balance with Class M weights was performed before each set was weighed, and a calibration check was made after each set. If they were off by more than $\pm 4 \mu\text{g}$, the entire set was reweighed. Out of each set, three filters were chosen at random for reweighing. If the reweights of each filter were not within $\pm 10 \mu\text{g}$ of their original value, the entire set was reweighed.

Data management in a study of this nature is a large and important task. All data transcribing operations were verified by checking 100% of the data. Computer entry of data was also verified by 100% checking. XRF data was processed by a dedicated on line computer, stored on floppy disks, and transferred to another computer for merging with other data by magnetic tape. NAA data was saved on digital cassette tapes, and directly transferred to the computer for processing.

Complete standard operating procedures for XRF, INAA and mass analyses as well as for all aspects of sample laboratory procedures are presented in Appendix A. Ambient volumes of air sampled were determined from field data sheets filled out by field operators. The Standard Operating Procedures and audits for the calculation of air volumes that were sampled are given in Appendices A and J.

Carbon analyses were conducted on a limited number of glass fiber filters. The samples were analyzed for organic and elemental carbon by a thermal-optical method which is described in Appendix C. Carbonate carbon analysis was performed by removing a 0.25 cm^2 disk from the filter, adding excess 1% phosphoric acid, reducing the CO_2 evolved to CH_4 by passing it through a nickel coated firebrick substrate in the presence of H_2 and finally by measuring the amount of methane with a flame ionization detector. All carbon analyses were carried out by the Oregon Graduate Center, Beaverton, Oregon.

Mass and elemental data for high volume filters were provided by the State of Montana. Atomic Absorption Spectrophotometry and Inductively-coupled argon plasma spectrophotometry (ICAP) were used to measure Pb, Cd, Cu, Zn and As concentrations.

2.4 The Chemical Mass Balance Receptor Modelling Technique

The identification of source contributions to TSP and Pb concentrations requires the application of a receptor model. The chemical mass balance receptor model has been demonstrated as being the most quantitative of the receptor models. The starting point for the Chemical Mass Balance (CMB) Model is essentially the same as the source (dispersion) model. The source model states that the contribution of a source to a receptor (i.e., some ambient sampling site) is dependent upon its emission rate and a dispersion factor. Limitations of dispersion modelling, however, arise from difficulty in quantifying dispersion factors in areas of complex terrain, variable meteorology, from difficulties in identifying emission rates and other operating parameters associated with emission sources. The advantage of the CMB, and other receptor approaches, is that an exact knowledge of these parameters is unnecessary.

The basic assumptions inherent in the CMB approach are similar to those associated with other receptor and source (dispersion) models. One principal assumption is that the particulate mass measured at the receptor is a direct, linear sum of the mass contribution from a number of specific sources, i.e.,

$$m = \sum_{j=1}^P M_j, \quad (1)$$

where,

m = measured mass concentration of particles from all "p" sources ($\mu\text{g}/\text{m}^3$), and

M_j = the mass impact at the receptor of source "j" ($\mu\text{g}/\text{m}^3$).

Similarly, the concentration of a given chemical species at an ambient sampling site is assumed to be the sum of the contributions from each individual source emitting that species,

$$C'_i = \sum_{j=1}^P F'_{ij} X_{ij} M_j, \quad (2)$$

where,

C'_i = measured concentration of species "i" from all sources "p" ($\mu\text{g}/\text{m}^3$),

F'_{ij} = the weight fraction of species "i" in the emissions of source "j" as measured at the source,

X_{ij} = the coefficient of fractionation of species "i" in the emissions of source "j". Fractionation is a systematic change in relative species abundances as the aerosol ages due, for example, to gravitational settling or condensation of volatile organic hydrocarbons, and

M_j = the mass impact at the receptor of source "j" ($\mu\text{g}/\text{m}^3$).

The F'_{ij} values associated with major emission sources are measured or adapted from literature values, and the C_i data are obtained through field monitoring programs. Under most circumstances, X_{ij} can be assumed to be close to unity, particularly if source and ambient samples are size classified and the source samples are collected at near ambient temperature (e.g., with a dilution sampler from industrial stacks). If X_{ij} is assumed to be unity, then,

$$F_{ij} = F'_{ij}, \quad (3)$$

where,

F_{ij} = the weight fraction of species "i" in the emissions of source "j" as received at the receptor.

By dividing both sides of equation (2) by the particulate mass collected at the receptor and by substituting F_{ij} for F'_{ij} , the following equation is obtained:

$$C_i = \sum_{j=1}^p F_{ij} S_j \quad (i=1 \text{ to } n) \quad (4)$$

where,

C_i = the total weight fraction of species "i" measured in ambient samples

$$(i.e., C_i = C'_i / \sum_{j=1}^p M_j),$$

F_{ij} = the weight fraction of species "i" in the emissions from source "j" received at the receptor, or as measured at the source when $X_{ij} = 1$,

S_j = the mass impact at the receptor of source "j" expressed as the weight fraction of the total mass collected at the receptor

$$(i.e., S_j = M_j / \sum_{j=1}^p M_j),$$

n = the number of chemical species considered, and

p = the number of sources impacting the receptor.

Since S_j is the quantity to be determined, a set of simultaneous summation equations can be written for all "i" species where "i" is defined as a "fitting" element. Once the set of equations are formed, the value of S_j can be solved by standard matrix manipulation techniques using linear least squares or effective variance solutions utilizing commonly available matrix mathematics. Figure 6 illustrates a simplified hypothetical set of CMB simultaneous equations. The effective variance least squares fitting method used by NEA, Inc. in this study weights the solution in accordance with uncertainties in both the source composition (F_{ij}) and the ambient aerosol species (C_i). The procedure ensures that those components with the greatest uncertainty receive less weight in the fit and that both sources of uncertainty are propagated through to the source impact (S_j) determination. It should also be noted that once S_j is determined for a source, its contribution to the ambient levels of a given chemical species (viz, Pb in this study) is a straight forward calculation since F_{ij} has been measured for each important source.

3.0 RESULTS AND DISCUSSION

The results of this study are presented in four sections. The results of the analyses of the East Helena ambient aerosol samples are presented in the first section. The rationale for selection of specific ambient data sets for detailed examination is also discussed in the first section. The second section contains the results of the analyses of source samples and discusses the formation of the source matrix subsequently used in the CMB modelling program. The differences, similarities and relative utility of the various source fingerprints is also discussed. The third section presents the final results of CMB source apportionment. Ambient data sets for CMB source apportionment were selected from sets which would be expected to regularly have ambient lead levels in excess of the federal primary lead standard and which had the highest TSP levels as well. The fourth and final section presents supplemental information. This includes particle size distribution, bivariate plots, data from other reports and general comments.

Figure 6

Simplified Hypothetical Set of CMB Simultaneous Equations

1. $C_{Al} = F_{Al, Auto} S_{Auto} + F_{Al, Road} S_{Road} + F_{Al, Smelt} S_{Smelt}$
2. $C_{Fe} = F_{Fe, Auto} S_{Auto} + F_{Fe, Road} S_{Road} + F_{Fe, Smelt} S_{Smelt}$
3. $C_{Cu} = F_{Cu, Auto} S_{Auto} + F_{Cu, Road} S_{Road} + F_{Cu, Smelt} S_{Smelt}$
4. $C_{Pb} = F_{Pb, Auto} S_{Auto} + F_{Pb, Road} S_{Road} + F_{Pb, Smelt} S_{Smelt}$

$i = Al, Fe, Cu \text{ and } Pb$

$n = 4$

$j = \text{automobile exhaust (auto), road dust (road) and smelter (smelt)}$

$p = 3$

Four equations in the form:

$$C_i = \sum_{j=1}^p F_{ij} S_j \quad (i = 1 \text{ to } n)$$

Four equations (four fitting elements) and three unknowns (S_{Auto} , S_{Road} and S_{Smelt})

S_{Auto} , S_{Road} and S_{Smelt} = weight fraction (or percent if desired) of mass of particles collected at an ambient sampling site originating from automobile exhaust, road dust and a smelter, respectively.

3.1 The Ambient Data Set

Due to the magnitude of the ambient data set produced in this study, reduction of the data into a usable format and selection of subsets to receive major emphasis was the first step in understanding the results of the study. To illustrate the magnitude of the ambient data set, it should be recalled that: (1) Mass and XRF analysis for 33 elements were conducted on nearly 700 teflon filters, (2) mass and lead values were reviewed from approximately 750 high volume filters and (3) cadmium, arsenic, copper and zinc values were also reviewed from approximately 190 high volume filters. This yields an ambient data set containing an estimated 26,760 datum points.

Data reduction was achieved in three principal ways: (1) Elements observed to be routinely below the XRF detection limits and/or at very low concentrations were not included in the CMB calculations, (2) quarterly mean concentration values by site and size category were calculated and detailed CMB modelling was conducted with these mean values, (3) after quarterly mean values were calculated and CMB modelling was conducted with them, key quarterly data sets were selected for additional examination and (4) co-collected samples were used in quarterly averages rather than all valid samples of each size category so that mass and elemental concentration data could be directly compared between the various size categories which were collected.

Tables 17 and 18 are examples of typical mass and elemental data measured on twenty-four hour samples. The uncertainties in Tables 17 and 18 are from the uncertainty in the volume of air sampled, the uncertainty associated with the determination of the mass of deposit and the analytical uncertainties associated with XRF analysis. Of the 33 elements measured and listed in Tables 17 and 18, five were not included in the CMB calculations due to their generally low ambient concentration and the consequent limited amount of insight that they provided. Those elements were Ga, Rb, Y, Zr and La. For the remaining 28 elements, arithmetic mean quarterly values for fine ($<2.5\mu$), coarse ($2.5-15\mu$) and low-volume TSP samples for each of the eleven sites are included in the CMB printouts in Appendix I (the MEAS. UG/M3 column). The uncertainties accompanying the mean elemental data are standard errors (standard deviation divided by \sqrt{n}). Mean values are compiled for each quarter for all valid samples and for those samples co-collected with hi-vol samples.

Table 17

Concentrations Measured on a Twenty-Four Hour
Ambient Sample - Canal Site

SAMPLE ID: 4/16/81 CANAL
PARTICLE SIZE: T
ANALYSIS ID: HT079

EXPOSED AREA: 13.80 SQUARE CM
MASS OF DEPOSIT: 2039+- 10 MICROGRAMS
VOLUME OF AIR SAMPLED: 45.80+- 4.58 CUBIC METERS
TOTAL SUSPENDED PARTICULATE: 44.5+- 4.5 UG/M3

ELEMENT	UG/CM2		UG/FILTER		PERCENT		UG/M3	
AL	7.639+-	0.476	105.417+-	6.568	5.170+-	0.323	2.302+-	0.271
SI	26.915+-	1.408	371.434+-	19.436	18.216+-	0.957	8.110+-	0.915
P	0.213+-	0.036	2.943+-	0.498	0.144+-	0.024	0.064+-	0.013
S	2.811+-	0.329	38.797+-	4.535	1.903+-	0.223	0.847+-	0.130
CL	0.347+-	0.087	4.790+-	1.202	0.235+-	0.059	0.105+-	0.028
K	1.588+-	0.119	21.910+-	1.648	1.075+-	0.081	0.478+-	0.060
CA	6.063+-	0.337	83.672+-	4.654	4.104+-	0.229	1.827+-	0.209
TI	0.384+-	0.036	5.301+-	0.498	0.260+-	0.024	0.116+-	0.016
V	0.022+-	0.011	0.304+-	0.150	0.015+-	0.007	0.007+-	0.003
CR	0.018+-	0.009	0.254+-	0.130	0.012+-	0.006	0.006+-	0.003
MN	0.138+-	0.015	1.900+-	0.206	0.093+-	0.010	0.041+-	0.006
FE	4.790+-	0.262	66.100+-	3.616	3.242+-	0.178	1.443+-	0.165
NI	0.039+-	0.009	0.541+-	0.130	0.027+-	0.006	0.012+-	0.003
CU	2.018+-	0.112	27.855+-	1.551	1.366+-	0.076	0.608+-	0.070
ZN	3.312+-	0.177	45.709+-	2.443	2.242+-	0.120	0.998+-	0.113
GA	0.006+-	0.014	0.089+-	0.189	0.004+-	0.009	0.002+-	0.004
AS	0.480+-	0.066	6.620+-	0.915	0.325+-	0.045	0.145+-	0.025
SE	0.017+-	0.006	0.228+-	0.088	0.011+-	0.004	0.005+-	0.002
BR	0.074+-	0.010	1.018+-	0.142	0.050+-	0.007	0.022+-	0.004
RB	0.005+-	0.008	0.069+-	0.109	0.003+-	0.005	0.002+-	0.002
SR	0.033+-	0.010	0.455+-	0.142	0.022+-	0.007	0.010+-	0.003
Y	0.003+-	0.013	0.045+-	0.180	0.002+-	0.009	0.001+-	0.004
ZR	0.000+-	0.042	0.000+-	0.582	0.000+-	0.029	0.000+-	0.013
PD	0.018+-	0.025	0.243+-	0.341	0.012+-	0.017	0.005+-	0.007
AG	0.054+-	0.034	0.746+-	0.475	0.037+-	0.023	0.016+-	0.011
CD	0.186+-	0.064	2.570+-	0.384	0.126+-	0.043	0.056+-	0.020
IN	0.099+-	0.061	1.364+-	0.840	0.067+-	0.041	0.030+-	0.019
SN	0.000+-	0.069	0.000+-	0.946	0.000+-	0.046	0.000+-	0.021
SB	0.108+-	0.142	1.493+-	1.964	0.073+-	0.096	0.033+-	0.043
BA	0.536+-	0.326	7.400+-	4.505	0.363+-	0.221	0.162+-	0.100
LA	0.116+-	0.450	1.606+-	6.216	0.079+-	0.305	0.035+-	0.136
HG	0.006+-	0.011	0.085+-	0.154	0.004+-	0.008	0.002+-	0.003
PB	3.098+-	0.173	42.751+-	2.388	2.097+-	0.118	0.933+-	0.107 - lead

Table 18

Concentrations Measured on a Twenty-Four Hour
Ambient Sample - Firehall Site

SAMPLE ID: 3/26/81 FIREH
PARTICLE SIZE: T
ANALYSIS ID: HT059

EXPOSED AREA: 13.85 SQUARE CM
MASS OF DEPOSIT: 3012+- 10 MICROGRAMS
VOLUME OF AIR SAMPLED: 44.00+- 4.40 CUBIC METERS
TOTAL SUSPENDED PARTICULATE: 68.5+- 6.8 UG/M3

ELEMENT	UG/CM2		UG/FILTER		PERCENT		UG/M3	
AL	5.392+-	0.291	74.678+-	4.035	2.479+-	0.134	1.697+-	0.193
SI	17.173+-	0.874	237.851+-	12.104	7.897+-	0.403	5.406+-	0.607
P	0.460+-	0.033	6.376+-	0.460	0.212+-	0.015	0.145+-	0.018
S	7.922+-	0.623	109.715+-	8.632	3.643+-	0.287	2.494+-	0.317
CL	0.808+-	0.092	11.187+-	1.279	0.371+-	0.042	0.254+-	0.039
K	2.019+-	0.116	27.961+-	1.605	0.928+-	0.053	0.635+-	0.073
CA	14.102+-	0.722	195.311+-	10.006	6.484+-	0.333	4.439+-	0.499
TI	0.269+-	0.019	3.723+-	0.270	0.124+-	0.009	0.085+-	0.010
V	0.029+-	0.006	0.406+-	0.080	0.013+-	0.003	0.009+-	0.002
CR	0.041+-	0.006	0.568+-	0.086	0.019+-	0.003	0.013+-	0.002
MN	0.222+-	0.014	3.076+-	0.201	0.102+-	0.007	0.070+-	0.008
FE	5.482+-	0.286	75.926+-	3.967	2.521+-	0.132	1.726+-	0.195
NI	0.168+-	0.015	2.326+-	0.207	0.077+-	0.007	0.053+-	0.007
CU	29.773+-	1.503	412.358+-	20.821	13.690+-	0.693	9.372+-	1.050
ZN	13.071+-	0.661	181.028+-	9.160	6.010+-	0.305	4.114+-	0.461
GA	0.073+-	0.020	1.015+-	0.278	0.034+-	0.009	0.023+-	0.007
AS	2.396+-	0.146	33.185+-	2.026	1.102+-	0.067	0.754+-	0.088
SE	0.041+-	0.008	0.574+-	0.110	0.019+-	0.004	0.013+-	0.003
BR	0.275+-	0.018	3.811+-	0.248	0.127+-	0.008	0.087+-	0.010
RB	0.000+-	0.007	0.000+-	0.094	0.000+-	0.003	0.000+-	0.002
SR	0.116+-	0.011	1.609+-	0.156	0.053+-	0.005	0.037+-	0.005
Y	0.000+-	0.014	0.000+-	0.196	0.000+-	0.007	0.000+-	0.004
ZR	0.000+-	0.035	0.000+-	0.481	0.000+-	0.016	0.000+-	0.011
PD	0.030+-	0.024	0.419+-	0.334	0.014+-	0.011	0.010+-	0.008
AG	0.082+-	0.033	1.133+-	0.453	0.038+-	0.015	0.026+-	0.011
CD	0.436+-	0.065	6.034+-	0.900	0.200+-	0.030	0.137+-	0.025
IN	0.109+-	0.051	1.503+-	0.703	0.050+-	0.023	0.034+-	0.016
SN	0.613+-	0.080	8.485+-	1.111	0.282+-	0.037	0.193+-	0.032
SB	0.484+-	0.122	6.705+-	1.689	0.223+-	0.056	0.152+-	0.041
BA	0.083+-	0.255	1.156+-	3.539	0.038+-	0.117	0.026+-	0.080
LA	0.000+-	0.381	0.000+-	5.271	0.000+-	0.175	0.000+-	0.120
HG	0.064+-	0.016	0.885+-	0.222	0.029+-	0.007	0.020+-	0.005
PB	9.964+-	0.510	138.000+-	7.060	4.582+-	0.235	3.136+-	0.352

For site 1 (Canal) only, in addition to the dichotomous/lo-vol/hi-vol co-collected sets, there are dichotomous/hi-vol co-collected sets and lo-vol/hi-vol co-collected sets. This was done since at the Canal site there were many dates when a dichotomous and a hi-vol sampler were run, but no valid lo-vol sample was obtained. Similarly, there were many dates when lo-vol and hi-vol samplers were run but no valid dichotomous sample was obtained. The Canal site was the only site that these special data sets were formed since at other sites generally both dichotomous and lo-vol samples were collected on the same day with the limiting factor being the simultaneous collection of a hi-vol sample. At several sites only a dichotomous sampler or only a lo-vol sampler was set up along with the hi-vol sampler. In those cases, dichotomous/hi-vol co-collected sets or lo-vol/hi-vol co-collected sets, respectively, were referred to as the co-collected samples.

Tables 19 through 29 represent a compilation of Mass, Pb and Cd data for each site by quarter for dichotomous, lo-vol and hi-vol samples. Mean values for all valid samples, co-collected sets as well as the special sets for Site 1 have been calculated. Table 30 is a compilation of Cu, Zn and As mean values for samples collected during the fourth quarter. Copper, zinc and arsenic values for hi-vol filters were available only for fourth quarter samples. As with Tables 19 through 29, Table 30 lists mean values for fine and coarse dichotomous filters, lo-vol samples and hi-vol samples. Both mean values for all valid samples and co-collected samples have been compiled.

By reviewing the mean quarterly lead values in Tables 19 through 29, it is clear that the Firehall, Hadfield, Hastie and Highway sites are where the federal quarterly standard for lead ($1.5 \mu\text{g}/\text{m}^3$) is likely to be regularly exceeded and in addition those sites also have the highest TSP levels. For these two reasons, those sites have been identified as the key sites for this report. In addition to the four aforementioned sites, the Muffick site was also selected as a key site, even though the mean hi-vol lead value ($1.29 \mu\text{g}/\text{m}^3$) from the seven samples collected there was less than the $1.5 \mu\text{g}/\text{m}^3$ standard and the arithmetic mean TSP value was relatively low. The Muffick site is geographically close to the Hadfield and Firehall sites and

Table 19

MASS, Pb and Cd MEAN VALUES AT SITE 1 (CANAL) BY QUARTER

	All Valid Samples Average \pm S.D. ($\mu\text{g}/\text{m}^3$)			Co-Collected Samples Average \pm S.D. ($\mu\text{g}/\text{m}^3$)			Special Samples Average \pm S.D. ($\mu\text{g}/\text{m}^3$)		
	Mass	Pb	Cd	Mass	Pb	Cd	Mass	Pb	Cd
1st Quarter									
F	(14) 10.6 \pm 7.4	.23 \pm .20	.043 \pm .079	(12) 11.5 \pm 7.5	.26 \pm .20	.050 \pm .084			
C	(14) 16.5 \pm 9.4	.27 \pm .23	.017 \pm .018	(12) 15.6 \pm 9.9	.30 \pm .24	.018 \pm .019			
L.V.	(17) 34.7 \pm 15.4	.61 \pm .61	.059 \pm .112	(12) 38.2 \pm 15.5	.77 \pm .67	.08 \pm .13			
H.V.	(19) 51 \pm 21	.92 \pm .73		(12) 51 \pm 19	1.01 \pm 0.80				
2nd Quarter									
F	(20) 4.95 \pm 2.57	.21 \pm .19	.038 \pm .062	(11) 5.39 \pm 3.30	.15 \pm .20	.019 \pm .030	(18) 4.96 \pm 2.7	.19 \pm .20	.038 \pm .065
C	(20) 11.5 \pm 17.5	.16 \pm .13	.009 \pm .012	(11) 12.9 \pm 23.9	.11 \pm .11	.007 \pm .009	(18) 11.7 \pm 18.5	.14 \pm .11	.010 \pm .013
L.V.	(19) 33.6 \pm 35.7	.54 \pm .55	.041 \pm .053	(11) 39.9 \pm 45.8	.54 \pm .64	.032 \pm .050	(17) 32.7 \pm 37.8	.49 \pm .56	.039 \pm .056
H.V.	(30) 44 \pm 38	.76 \pm .82		(11) 57 \pm 60	.93 \pm 1.19		(18) 50 \pm 48	.90 \pm .95	
							(17) 48 \pm 49	.80 \pm 1.01	
3rd Quarter									
F	(10) 7.97 \pm 4.00	.18 \pm .25	.019 \pm .026	(5) 8.92 \pm 5.59	.13 \pm .05	.017 \pm .019	(9) 8.03 \pm 4.24	.19 \pm .26	.018 \pm .027
C	(10) 17.4 \pm 9.8	.098 \pm .070	.001 \pm .004	(5) 16.1 \pm 10.5	.063 \pm .011	.002 \pm .005	(9) 16.5 \pm 9.9	.096 \pm .074	.001 \pm .004
L.V.	(12) 43.6 \pm 18.3	.28 \pm .16	.054 \pm .123	(5) 49.2 \pm 22.1	.30 \pm .07	.024 \pm .027	(11) 43.5 \pm 19.2	.29 \pm .16	.058 \pm .128
H.V.	(28) 77 \pm 68	.77 \pm 1.42		(5) 80 \pm 25	.64 \pm .15		(9) 74 \pm 25	.77 \pm .50	
							(11) 71 \pm 19	.56 \pm .27	
4th Quarter									
F									
C									
L.V.									
H.V.	(14) 53 \pm 24	1.09 \pm .79	(12) .143 \pm .190						

Numbers in parenthesis preceding values are number of samples. The number of samples on which Pb and Cd measurements were made are the same as samples on which mass was determined unless otherwise noted.

*Dichot co-collected with hi-vol.

ΔLo-vol co-collected with hi-vol.

Table 20

MASS, Pb and Cd MEAN VALUES AT SITE 2 (Dartman) BY QUARTER

	All Valid Samples Average \pm S.D. ($\mu\text{g}/\text{m}^3$)			Co-Collected Samples Average \pm S.D. ($\mu\text{g}/\text{m}^3$)		
	Mass	Pb	Cd	Mass	Pb	Cd
1st Quarter F C L.V. H.V.						
2nd Quarter F C L.V. H.V.						
3rd Quarter F C L.V. H.V.						
	(10) 72 \pm 31	3.55 \pm 3.96	.288 \pm .280			
4th Quarter F C L.V. H.V.						
	(26) 27.5 \pm 17.3	.93 \pm .77	.12 \pm .11	(26) 27.5 \pm 17.3	.93 \pm .77	.12 \pm .11
	(29) 44 \pm 23	1.29 \pm 1.06	.141 \pm .169	(26) 46 \pm 23	1.34 \pm 1.09	.150 \pm .176

Numbers in parenthesis preceeding values are number of samples. The number of samples on which Pb and Cd measurements were made are the same as samples on which mass was determined unless otherwise noted.

Table 21

MASS, Pb and Cd MEAN VALUES AT SITE 3 (Firehall) BY QUARTER

over std.

	All Valid Samples Average \pm S.D. ($\mu\text{g}/\text{m}^3$)			Co-Collected Samples Average \pm S.D. ($\mu\text{g}/\text{m}^3$)		
	Mass	Pb	Cd	Mass	Pb	Cd
1st Quarter						
F	(16) 14.1 \pm 8.5	.85 \pm .84	.121 \pm .141	(13) 13.6 \pm 8.0	.97 \pm .88	.13 \pm .15
C	(16) 13.8 \pm 8.6	.48 \pm .39	.025 \pm .024	(13) 13.4 \pm 7.9	.50 \pm .40	.026 \pm .024
L.V.	(17) 82.4 \pm 34.4	5.41 \pm 3.83	.49 \pm .50	(13) 79.1 \pm 27.7	5.61 \pm 3.90	.52 \pm .55
H.V.	(20) 102 \pm 50	6.20 \pm 4.26		(13) 98 \pm 30	6.89 \pm 4.33	
H.V. Colocated	(18) 113 \pm 50	6.91 \pm 4.83		(12) 107 \pm 35	7.52 \pm 5.08	
2nd Quarter						
F	(13) 20.1 \pm 37.6	.60 \pm 1.20	.069 \pm .129	(9) 25.9 \pm 44.4	.72 \pm 1.43	.087 \pm .153
C	(13) 7.5 \pm 5.82	.12 \pm .12	.006 \pm .012	(9) 8.89 \pm 6.47	.14 \pm .12	.009 \pm .013
L.V.	(11) 62.8 \pm 46.5	2.46 \pm 3.35	.22 \pm .33	(9) 65.6 \pm 53.6	2.11 \pm 3.58	.19 \pm .36
H.V.	(14) 83 \pm 54	2.89 \pm 3.47		(9) 86 \pm 63	2.70 \pm 4.26	
H.V. Colocated	(14) 91 \pm 60	2.94 \pm 3.39		(9) 91 \pm 68	2.71 \pm 4.16	
3rd Quarter						
F						
C						
L.V.						
H.V.						
4th Quarter						
F						
C						
L.V.						
H.V.						

Numbers in parenthesis preceeding values are number of samples. The number of samples on which Pb and Cd measurements were made are the same as samples on which mass was determined unless otherwise noted.

0030533

Table 22

MASS, Pb and Cd MEAN VALUES AT SITE 4 (Hadfield) BY QUARTER

	All Valid Samples Average \pm S.D. ($\mu\text{g}/\text{m}^3$)			Co-Collected Samples Average \pm S.D. ($\mu\text{g}/\text{m}^3$)		
	Mass	Pb	Cd	Mass	Pb	Cd
1st Quarter						
F						
C						
L.V.						
H.V.						
2nd Quarter						
F						
C						
L.V.						
H.V.						
3rd Quarter						
F	(8) 11.2 \pm 3.2	.82 \pm .66	.125 \pm .115	(7) 10.6 \pm 2.8	.72 \pm .64	.12 \pm .12
C	(8) 14.4 \pm 11.3	.43 \pm .30	.014 \pm .017	(7) 13.1 \pm 11.6	.36 \pm .23	.013 \pm .019
L.V.	(11) 54.9 \pm 27.1	1.96 \pm 1.38	.18 \pm .14	(7) 43.6 \pm 18.8	1.43 \pm .76	.13 \pm .07
H.V.	(15) 117 \pm 55	4.99 \pm 2.68		(7) 84 \pm 33	3.28 \pm 1.87	
H.V. Colocated	(15) 118 \pm 54	5.06 \pm 2.76		(7) 82 \pm 35	3.26 \pm 1.90	
4th Quarter						
F	(30) 14.9 \pm 9.7	.43 \pm .33	.090 \pm .097	(28) 15.5 \pm 9.8	.45 \pm .33	.095 \pm .099
C	(30) 13.7 \pm 10.2	.40 \pm .36	.032 \pm .040	(28) 14.2 \pm 10.4	.42 \pm .36	.033 \pm .041
L.V.	(30) 49.2 \pm 23.5	1.51 \pm 1.08	.18 \pm .21	(28) 50.5 \pm 23.7	1.56 \pm 1.10	.18 \pm .21
H.V.	(28) 76 \pm 32	2.27 \pm 1.52	(25) .170 \pm .185	(28) 76 \pm 32	2.27 \pm 1.52	(25) .170 \pm .185
H.V. Colocated	(30) 77 \pm 32	2.22 \pm 1.49	(27) .180 \pm .184	(28) 77 \pm 32	2.22 \pm 1.49	(27) .180 \pm .184

over
std.

Numbers in parenthesis preceeding values are number of samples. The number of samples on which Pb and Cd measurements were made are the same as samples on which mass was determined unless otherwise noted.

0030534

Table 23

MASS, Pb and Cd MEAN VALUES AT SITE 5 (Hastie) BY QUARTER

	All Valid Samples Average \pm S.D. ($\mu\text{g}/\text{m}^3$)			Co-Collected Samples Average \pm S.D. ($\mu\text{g}/\text{m}^3$)		
	Mass	Pb	Cd	Mass	Pb	Cd
1st Quarter						
F						
C						
L.V.						
H.V.	(20) 76 \pm 38	3.19 \pm 3.72				
2nd Quarter						
F						
C						
L.V.						
H.V.	(29) 77 \pm 56	1.60 \pm 1.47				
3rd Quarter						
F						
C						
L.V.						
H.V.	(25) 85 \pm 37	2.34 \pm 2.14				
4th Quarter						
F	(26) 19.2 \pm 12.7	.67 \pm .44	.14 \pm .13	(23) 20.4 \pm 13.0	.72 \pm .44	.14 \pm .14
C	(26) 16.9 \pm 10.9	.66 \pm .51	.051 \pm .032	(23) 18.0 \pm 11.1	.73 \pm .51	.054 \pm .032
L.V.	(27) 45.0 \pm 19.8	1.72 \pm 1.00	.20 \pm .13	(23) 45.0 \pm 21.2	1.82 \pm 1.01	.21 \pm .13
H.V.	(26) 69 \pm 30	2.51 \pm 1.52	(23) .191 \pm .146	(23) 69 \pm 29	2.56 \pm 1.57	(21).201 \pm .149

Numbers in parenthesis preceeding values are number of samples. The number of samples on which Pb and Cd measurements were made are the same as samples on which mass was determined unless otherwise noted.

over

Table 24

MASS, Pb and Cd MEAN VALUES AT SITE 6 (Highway) BY QUARTER

	All Valid Samples Average \pm S.D. ($\mu\text{g}/\text{m}^3$)			Co-Collected Samples Average \pm S.D. ($\mu\text{g}/\text{m}^3$)		
	Mass	Pb	Cd	Mass	Pb	Cd
1st Quarter F C L.V. H.V.						
2nd Quarter F C L.V. H.V.						
3rd Quarter F C L.V. H.V. H.V. Colocated	(3) 108 \pm 51 (3) 107 \pm 45	5.33 \pm 2.42 5.36 \pm 2.05				
4th Quarter F C L.V. H.V.	(23) 67.4 \pm 31.8	2.04 \pm 1.32	.21 \pm .16			

Numbers in parenthesis preceeding values are number of samples. The number of samples on which Pb and Cd measurements were made are the same as samples on which mass was determined unless otherwise noted.

Over

Table 25

MASS, Pb and Cd MEAN VALUES AT SITE 7 (Microwave) BY QUARTER

	All Valid Samples Average \pm S.D. ($\mu\text{g}/\text{m}^3$)			Co-Collected Samples Average \pm S.D. ($\mu\text{g}/\text{m}^3$)		
	Mass	Pb	Cd	Mass	Pb	Cd
1st Quarter						
F						
C						
L.V.						
H.V.						
2nd Quarter						
F	(6) 2.17 \pm .69	.024 \pm .028	0 \pm 0	(6) 2.17 \pm .69	.024 \pm .028	0 \pm 0
C	(6) 3.68 \pm 1.64	.016 \pm .024	0 \pm 0	(6) 3.68 \pm 1.64	.016 \pm .024	0 \pm 0
L.V.						
H.V.	(23) 21 \pm 10	.11 \pm .09		(6) 17 \pm 7	.12 \pm .10	
3rd Quarter						
F	(3) 6.17 \pm 3.35	.163 \pm .091	.035 \pm .045	(3) 6.17 \pm 3.35	.163 \pm .091	.035 \pm .045
C	(3) 9.81 \pm 10.2	.062 \pm .042	.006 \pm .011	(3) 9.81 \pm 10.2	.062 \pm .042	.006 \pm .011
L.V.						
H.V.	(22) 36 \pm 10	.17 \pm .14		(3) 33 \pm 16	.33 \pm .18	
4th Quarter						
F						
C						
L.V.						
H.V.	(14) 25 \pm 12	.19 \pm .24	(12) .033 \pm .041			

Numbers in parenthesis preceeding values are number of samples. The number of samples on which Pb and Cd measurements were made are the same as samples on which mass was determined unless otherwise noted.

Table 26

MASS, Pb and Cd MEAN VALUES AT SITE 9 (Muffick) BY QUARTER

	All Valid Samples Average \pm S.D. ($\mu\text{g}/\text{m}^3$)			Co-Collected Samples Average \pm S.D. ($\mu\text{g}/\text{m}^3$)		
	Mass	Pb	Cd	Mass	Pb	Cd
1st Quarter						
F						
C						
L.V.						
H.V.						
2nd Quarter						
F	(7) 5.65 \pm 1.92	.19 \pm .19	.002 \pm .006	(6) 5.80 \pm 2.11	.22 \pm .19	.044 \pm .060
C	(7) 32.0 \pm 62.2	.13 \pm .13	.004 \pm .010	(6) 8.55 \pm 5.24	.15 \pm .14	.004 \pm .011
L.V.	(6) 41.2 \pm 8.9	.86 \pm .29	.11 \pm .21	(6) 41.2 \pm 8.9	.86 \pm .79	.11 \pm .21
H.V.	(7) 55 \pm 15	1.29 \pm 1.45		(6) 57 \pm 16	1.41 \pm 1.56	
H.V. Colocated	(7) 57 \pm 15	1.31 \pm 1.35		(6) 60 \pm 14	1.44 \pm 1.43	
3rd Quarter						
F						
C						
L.V.						
H.V.						
4th Quarter						
F						
C						
L.V.						
H.V.						

Numbers in parenthesis preceeding values are number of samples. The number of samples on which Pb and Cd measurements were made are the same as samples on which mass was determined unless otherwise noted.

Table 27

MASS, Pb and Cd MEAN VALUES AT SITE 10 (Padbury) BY QUARTER

	All Valid Samples Average \pm S.D. ($\mu\text{g}/\text{m}^3$)			Co-Collected Samples Average \pm S.D. ($\mu\text{g}/\text{m}^3$)		
	Mass	Pb	Cd	Mass	Pb	Cd
1st Quarter						
F						
C						
L.V.						
H.V.						
2nd Quarter						
F						
C						
L.V.	(7) 11.7 \pm 2.7	.018 \pm .010	0 \pm 0	(7) 11.7 \pm 2.7	.018 \pm .010	0 \pm 0
H.V.	(11) 25 \pm 11	(10) .10 \pm .07		(7) 18 \pm 3	(6) .07 \pm .07	
3rd Quarter						
F						
C						
L.V.	(11) 44.8 \pm 25.2	.16 \pm .10	.012 \pm .021	(11) 44.8 \pm 25.2	.16 \pm .10	.012 \pm .021
H.V.	(27) 50 \pm 26	.17 \pm .11		(11) 67 \pm 34	.21 \pm .12	
4th Quarter						
F						
C						
L.V.	(27) 22.4 \pm 15.6	.19 \pm .18	.016 \pm .023	(25) 22.4 \pm 15.6	.19 \pm .18	.016 \pm .023
H.V.	(26) 37 \pm 25	.28 \pm .27	(23) .018 \pm .016	(25) 35 \pm 23	.26 \pm .25	(22) .018 \pm .013

Numbers in parenthesis preceeding values are number of samples. The number of samples on which Pb and Cd measurements were made are the same as samples on which mass was determined unless otherwise noted.

Table 28

MASS, Pb and Cd MEAN VALUES AT SITE 11 (South) BY QUARTER

	All Valid Samples Average \pm S.D. ($\mu\text{g}/\text{m}^3$)			Co-Collected Samples Average \pm S.D. ($\mu\text{g}/\text{m}^3$)		
	Mass	Pb	Cd	Mass	Pb	Cd
1st Quarter						
F						
C						
L.V.						
H.V.						
2nd Quarter						
F						
C						
L.V.						
H.V.	(14) 38 \pm 21	1.15 \pm 1.29				
3rd Quarter						
F						
C						
L.V.						
H.V.	(29) 59 \pm 23	1.41 \pm 1.32				
4th Quarter						
F	(29) 11.3 \pm 12.6	.31 \pm .42	.080 \pm .105	(28) 11.3 \pm 12.6	.31 \pm .42	.080 \pm .105
C	(29) 9.86 \pm 8.41	.26 \pm .40	.028 \pm .042	(28) 9.86 \pm 8.41	.26 \pm .40	.028 \pm .042
L.V.	(28) 24.7 \pm 19.0	.73 \pm 1.04	.10 \pm .14	(28) 24.7 \pm 19.0	.73 \pm 1.04	.10 \pm .14
H.V.	(30) 40 \pm 25	.94 \pm 1.20	(27) .098 \pm .114	(28) 40 \pm 26	.95 \pm 1.24	(25) .101 \pm .118

Numbers in parenthesis preceeding values are number of samples. The number of samples on which Pb and Cd measurements were made are the same as samples on which mass was determined unless otherwise noted.

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Table 29

MASS, Pb and Cd MEAN VALUES AT SITE 12 (Vollmer) BY QUARTER

	All Valid Samples Average \pm S.D. ($\mu\text{g}/\text{m}^3$)			Co-Collected Samples Average \pm S.D. ($\mu\text{g}/\text{m}^3$)		
	Mass	Pb	Cd	Mass	Pb	Cd
1st Quarter						
F						
C						
L.V.	(10) 27.6 \pm 13.6	.53 \pm .50	.044 \pm .057	(10) 27.6 \pm 13.6	.53 \pm .50	.044 \pm .057
H.V.	(13) 39 \pm 17	.67 \pm .46		(10) 37 \pm 16	.59 \pm .43	
2nd Quarter						
F						
C						
L.V.	(16) 22.7 \pm 31.3	.24 \pm .17	.020 \pm .023	(15) 22.7 \pm 31.3	.24 \pm .17	.020 \pm .023
H.V.	(31) 36 \pm 32	.43 \pm .26		(15) 37 \pm 40	.39 \pm .25	
3rd Quarter						
F						
C						
L.V.	(16) 48.2 \pm 37.4	.30 \pm .31	.027 \pm .035	(16) 48.2 \pm 37.4	.30 \pm .31	.027 \pm .035
H.V.	(28) 55 \pm 33	.69 \pm .80		(16) 63 \pm 39	.64 \pm .74	
4th Quarter						
F						
C						
L.V.						
H.V.	(13) 38 \pm 16	1.27 \pm 1.39	(11) .087 \pm .113			

Numbers in parenthesis preceeding values are number of samples. The number of samples on which Pb and Cd measurements were made are the same as samples on which mass was determined unless otherwise noted.

Table 30

Cu, Zn and As--4th QUARTER MEAN CONCENTRATIONS ($\mu\text{g}/\text{m}^3$)

Site	Type	All Valid Samples				Co-Collected Samples			
		No.	Mean \pm Std. Dev.			No.	Mean \pm Std. Dev.		
			Cu	Zn	As		Cu	Zn	As
Canal	H.V.	12 ^a	0.83 \pm 0.60	0.73 \pm 0.89	0.073 \pm 0.067	-	-	-	-
Dartman	L.V.	29	1.31 \pm 1.44	0.59 \pm 0.47	0.154 \pm 0.140	26	1.31 \pm 1.44	0.59 \pm 0.47	0.154 \pm 0.140
	H.V.	29	2.02 \pm 2.39	0.82 \pm 0.51	0.122 \pm 0.100	26	2.20 \pm 2.46	0.83 \pm 0.54	0.126 \pm 0.104
Hadfield	F	30	0.175 \pm 0.203	0.334 \pm 0.296	0.107 \pm 0.099	28	0.181 \pm 0.212	0.335 \pm 0.302	0.110 \pm 0.101
	C	30	0.552 \pm 0.707	0.297 \pm 0.323	0.045 \pm 0.038	28	0.577 \pm 0.725	0.302 \pm 0.333	0.046 \pm 0.042
	L.V.	30 ^b	1.955 \pm 2.054	1.067 \pm 1.151	0.208 \pm 0.158	28	2.021 \pm 2.111	1.076 \pm 1.191	0.214 \pm 0.164
	H.V.w.	25 ^b	3.04 \pm 3.52	1.01 \pm 0.74	0.161 \pm 0.123	25 ^b	3.04 \pm 3.52	1.01 \pm 0.74	0.161 \pm 0.123
	H.V.e.	25 ^b	3.48 \pm 4.06	1.14 \pm 0.80	0.202 \pm 0.124	25 ^b	3.48 \pm 4.06	1.14 \pm 0.80	0.202 \pm 0.124
Hastie	F	26	0.255 \pm .301	0.770 \pm 0.479	0.237 \pm 0.316	23	0.277 \pm 0.316	0.838 \pm 0.465	0.258 \pm 0.173
	C	26	0.757 \pm .714	0.630 \pm 0.428	0.082 \pm 0.066	23	0.801 \pm 0.748	0.686 \pm 0.427	0.091 \pm 0.062
	L.V.	27	1.908 \pm 1.595	1.573 \pm 0.899	0.345 \pm 0.229	23	1.926 \pm 1.650	1.705 \pm 0.868	0.376 \pm 0.225
	H.V.	23 ^b	3.58 \pm 3.08	1.69 \pm 1.07	0.272 \pm 0.177	21 ^b	3.45 \pm 3.13	1.78 \pm 1.07	0.283 \pm 0.180
Highway	L.V.	23	13.38 \pm 12.26	1.33 \pm 0.79	0.341 \pm 0.244	-	-	-	-
Microwave	H.V.	12 ^a	0.30 \pm 0.16	0.18 \pm 0.21	0.014 \pm 0.015	-	-	-	-
Padbury	L.V.	27	0.031 \pm 0.031	0.088 \pm 0.083	0.024 \pm 0.026	25	0.033 \pm 0.035	0.093 \pm 0.085	0.025 \pm 0.030
	H.V.	23 ^b	0.19 \pm 0.07	0.20 \pm 0.29	0.023 \pm 0.020	22 ^b	0.12 \pm 0.06	0.17 \pm 0.27	0.022 \pm 0.019
South	F	29	0.044 \pm 0.081	0.172 \pm 0.194	0.080 \pm 0.108	28	0.046 \pm 0.0793	0.170 \pm 0.201	0.081 \pm 0.111
	C	29	0.139 \pm 0.301	0.143 \pm 0.194	0.027 \pm 0.043	28	0.143 \pm 0.307	0.145 \pm 0.201	0.028 \pm 0.042
	L.V.	28 ^b	0.291 \pm 0.539	0.375 \pm 0.455	0.113 \pm 0.148	28	0.291 \pm 0.539	0.375 \pm 0.045	0.113 \pm 0.148
	H.V.	27 ^b	0.52 \pm 0.70	0.54 \pm 0.53	0.108 \pm 0.113	25 ^b	0.54 \pm 0.72	0.55 \pm 0.55	0.109 \pm 0.116
Vollmer	H.V.	11 ^a	0.46 \pm 0.32	0.58 \pm 0.58	0.059 \pm 0.062	-	-	-	-

a. The mean does not include 10/1 or 10/7 hi-vol samples collected.

b. The mean does not include 10/1, 10/4 or 10/7 hi-vol samples collected.

the samples collected there are temporally between the shut-down of the Firehall site and the start-up of the Hadfield site. Figures 7 through 11 graphically illustrate the hi-vol lead data obtained at each of the five key sites during 1981.

The Key Mean Data sets for the five sites are listed in Table 31. Samples were collected at the Firehall site during the first and second quarters, at the Muffick site during the second quarter only, at the Hadfield site during the third and fourth quarters and at the Hastie and Highway sites during the fourth quarter. The number of valid and co-collected samples used to calculate the mean values is also listed in Table 31. There are no co-collected sample sets for the fourth quarter Highway site since no hi-vol samples were collected there during that period. A total of seven key mean data sets were formed from samples collected from the five sites.

Co-collected data sets were used where possible in the interpretation of the results so that the CMB source apportionment information as well as elemental and mass data could be compared across all size fractions for a given quarterly mean. To insure that the subset of hi-vol filters that were co-collected with dichotomous and/or lo-vol samples provided Pb and TSP concentrations representative of all valid hi-vol filters collected during the quarter, plots of TSP and lead values determined from both all valid and co-collected hi-vol samples were constructed for the key mean data sets with the exception of the Highway site which had no hi-vol data (Figures 12 and 13). Correlation between co-collected and all valid sample Pb means is particularly important since quarterly mean Pb values used for regulatory purposes are based on all valid hi-vol samples collected during the quarter. As can be seen from Figures 12 and 13, both Pb and TSP values calculated from co-collected and all valid samples compare favorably except for the Hadfield site, third quarter. The co-collected samples make up less than one-half of the total number of valid samples collected during that quarter at the Hadfield site and a number of the days not included in the co-collected data subset were high lead and mass impact days. The probable effect of using the co-collected data set for source apportionment

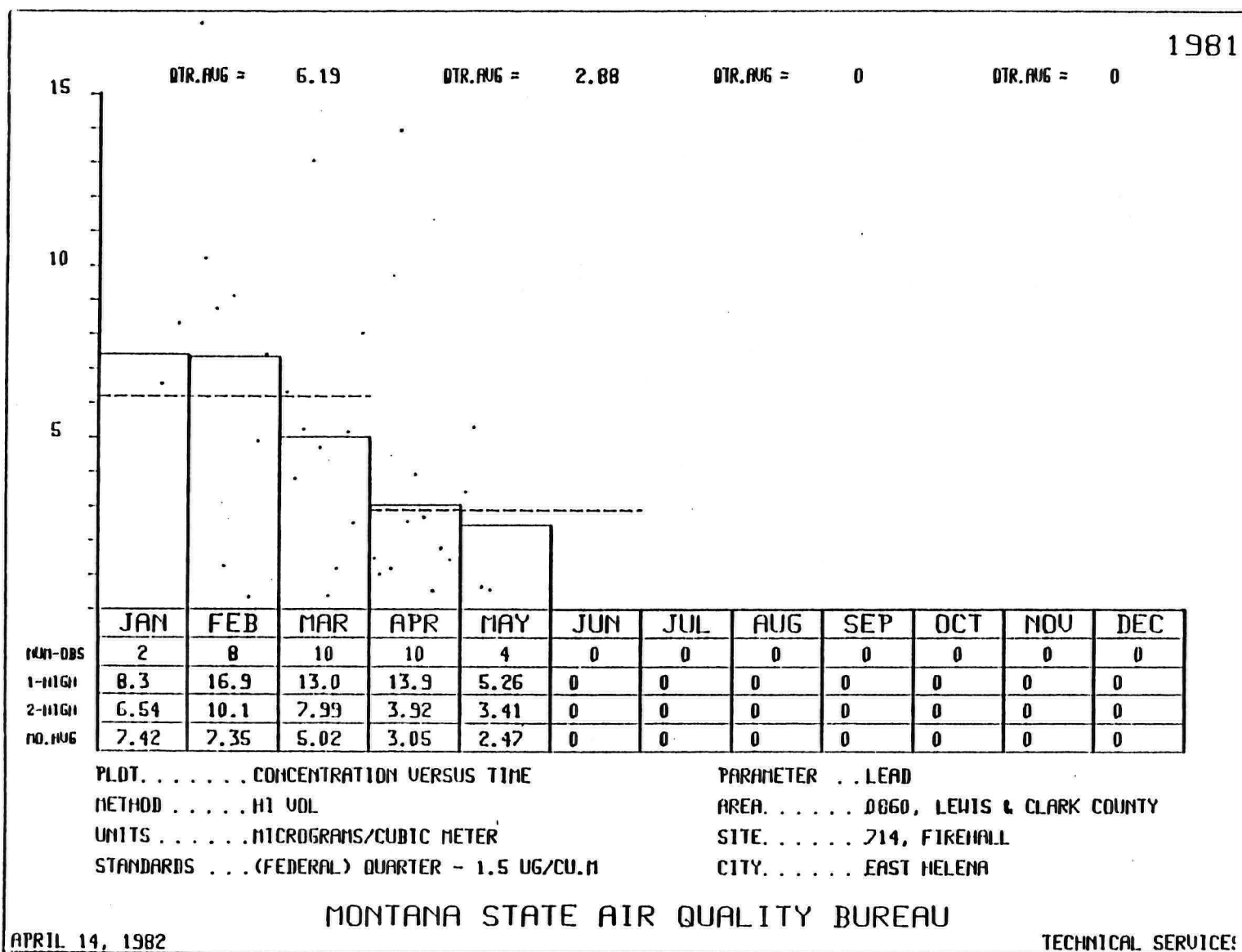


Figure 7 Ambient Lead Concentrations Measured on Hi-Vol Samples--Firehall Site, 1981

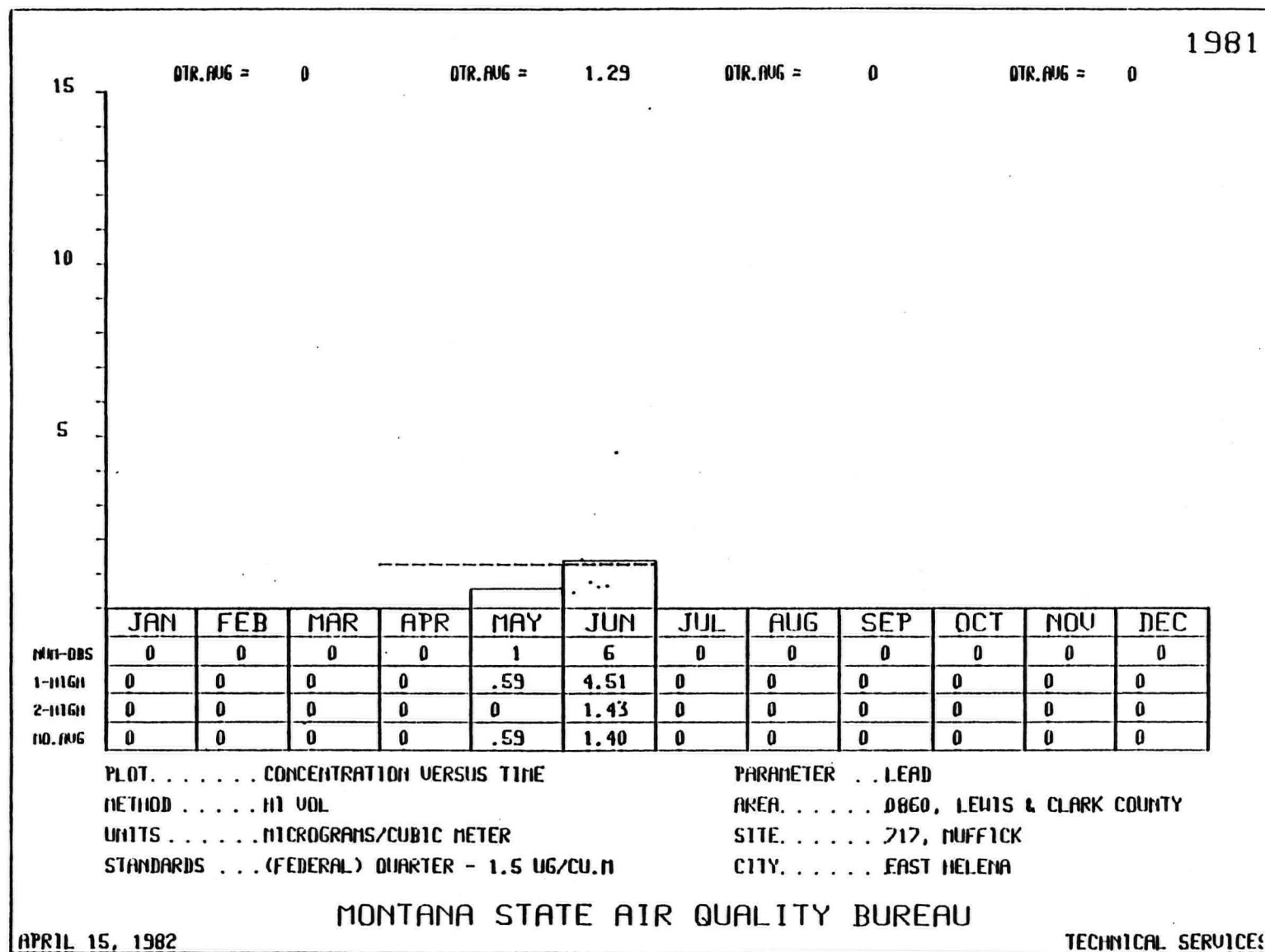


Figure 8 Ambient Lead Concentrations Measured on Hi-Vol Samples--Muffick Site, 1981

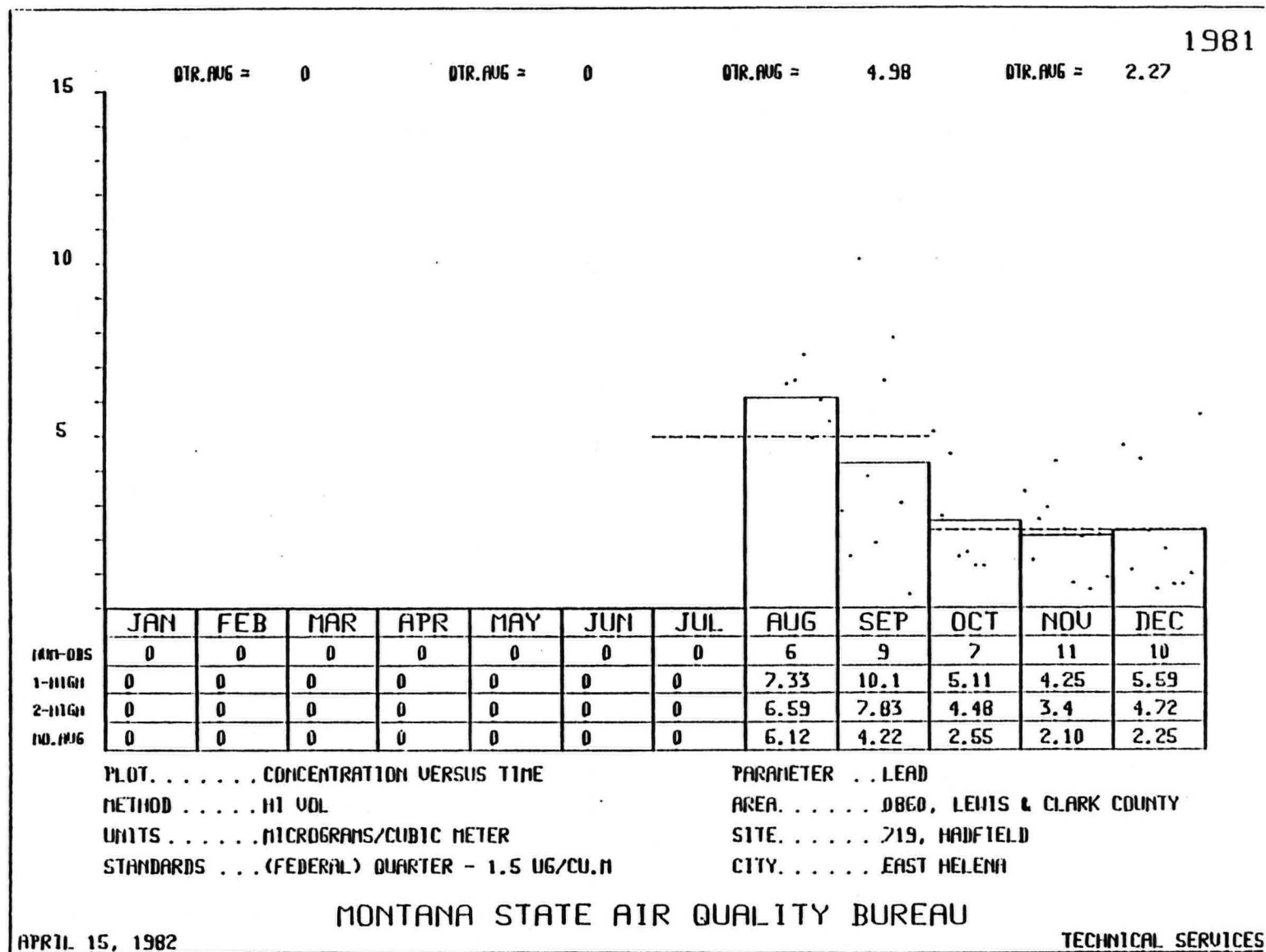


Figure 9 Ambient Lead Concentrations Measured on Hi-Vol Samples--Hadfield Site, 1981

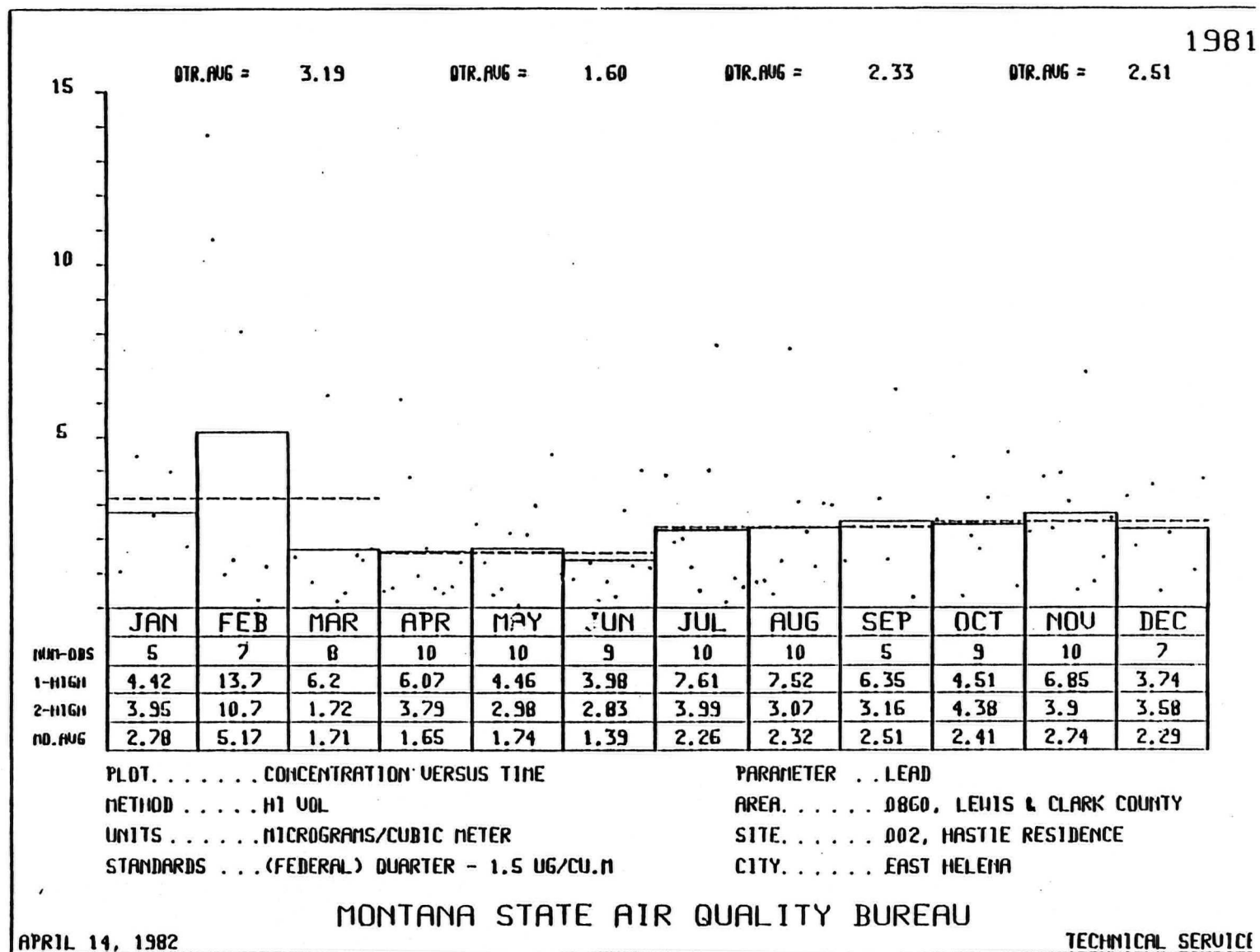
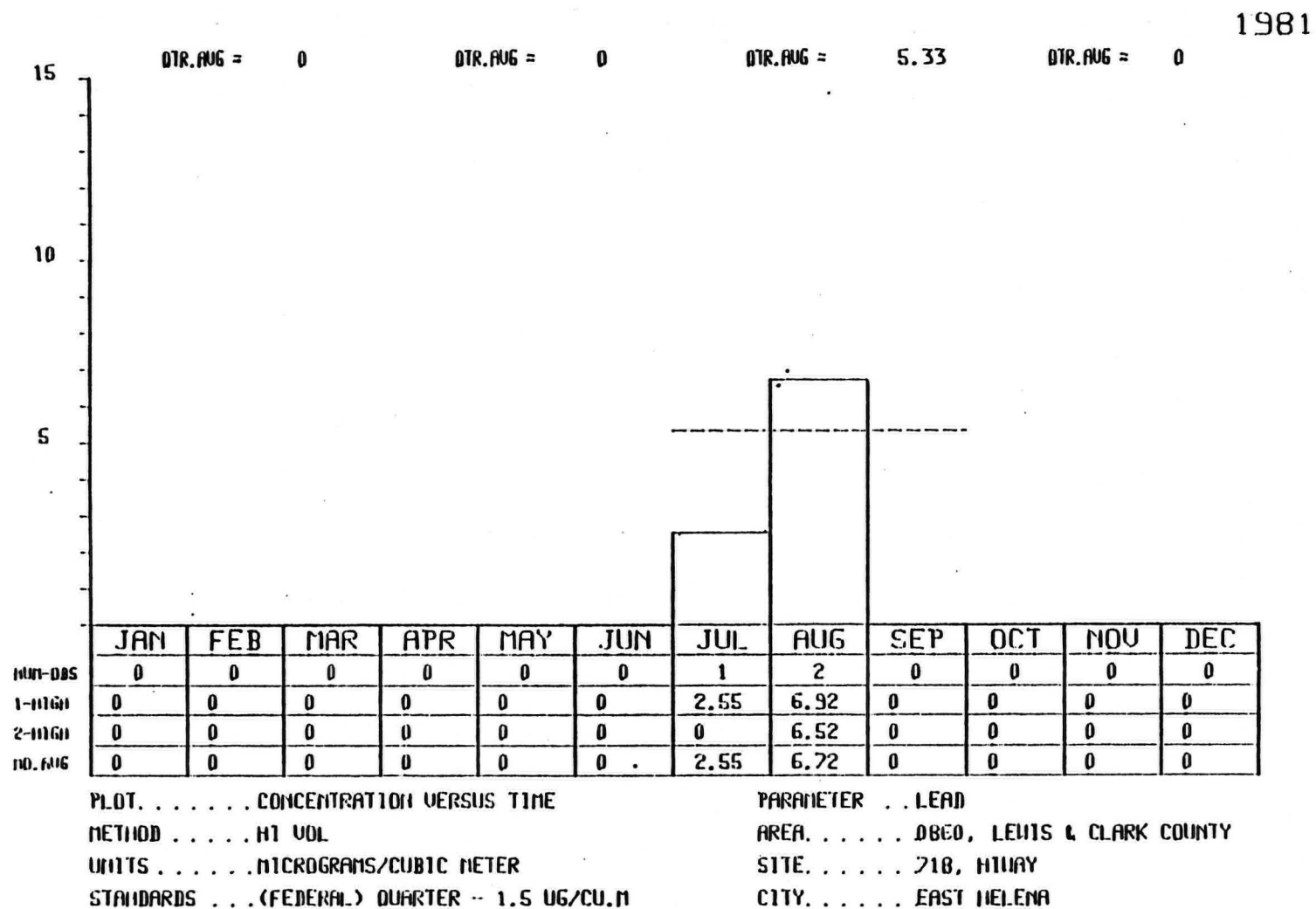


Figure 10 Ambient Lead Concentrations Measured on Hi-Vol Samples--Hastie Site, 1981



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Figure 11 Ambient Lead Concentrations Measured on Hi-Vol Samples--Highway Site, 1981

Table 31

KEY MEAN DATA SETS - AREAS OF HIGHEST AMBIENT LEAD CONCENTRATIONS

SITE NAME	QUARTER*	n, ALL VALID SAMPLES**	n, CO-COLLECTED SAMPLES
Firehall	1	D = 16, L = 17, H = 20	13
Firehall	2	D = 13, L = 11, H = 14	9
Muffick	2	D = 7, L = 6, H = 7	6
Hadfield	3	D = 8, L = 11, H = 15	7
Hadfield	4	D = 30, L = 30, H = 28	28
Hastie	4	D = 26, L = 27, H = 26	23
Highway	4	D = 0, L = 23, H = 0	0

*First Quarter Firehall samples started January 21, Second Quarter Firehall samples ran through May 10 only, Second Quarter Muffick samples ran from June 3 to June 18 only, Third Quarter Hadfield sampling started August 23.

** D = dichotomous samples
 L = lo-volume TSP samples
 H = hi-volume TSP samples

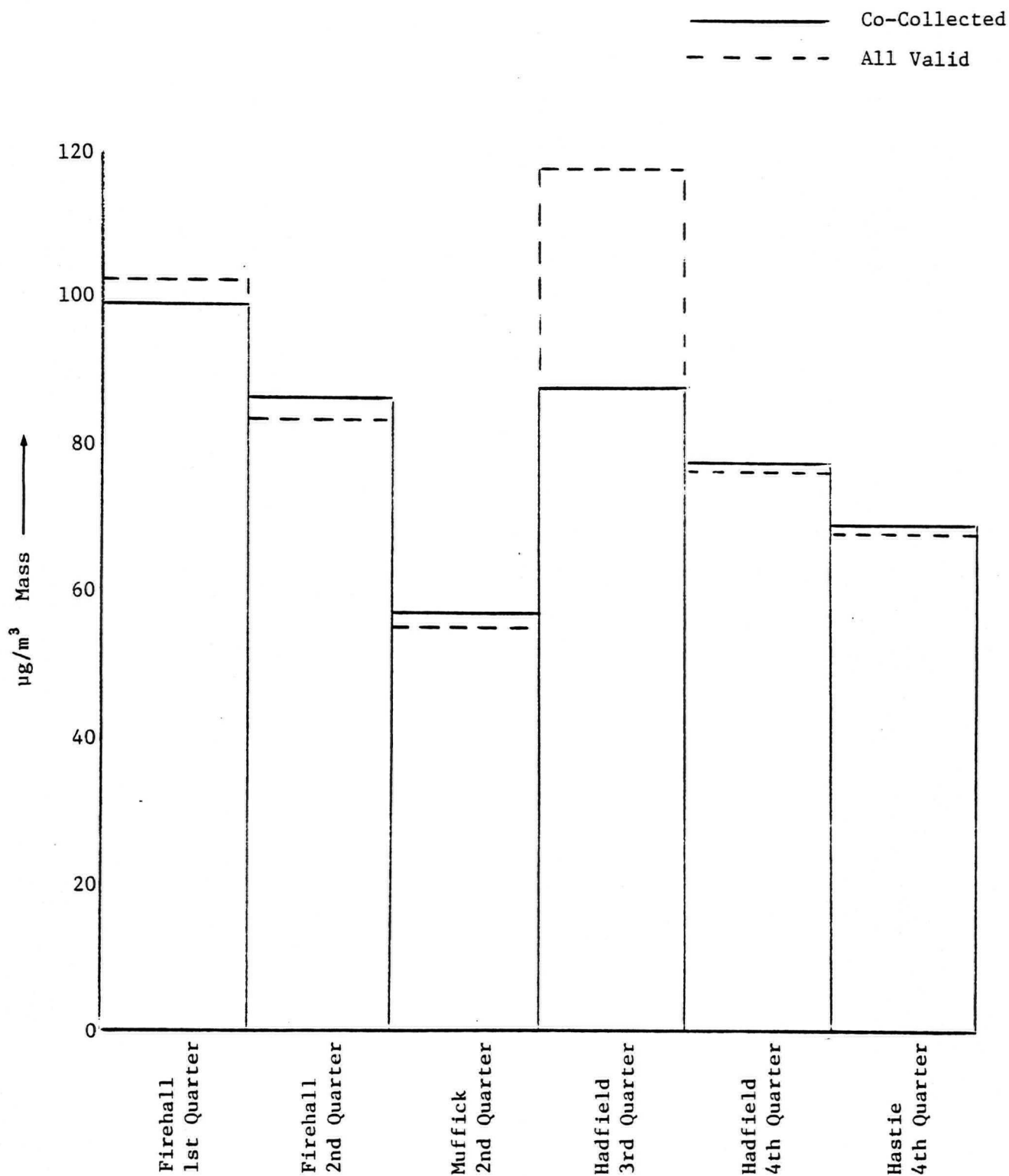


Figure 12

COMPARISON OF MEAN QUARTERLY TSP VALUES DETERMINED FOR ALL VALID HI-VOLUME SAMPLES VERSUS MEAN VALUES DETERMINED FROM THE SUBSET OF HI-VOLUME SAMPLES COLLECTED SIMULTANEOUSLY WITH LOW-VOLUME AND DICHOTOMOUS SAMPLES.

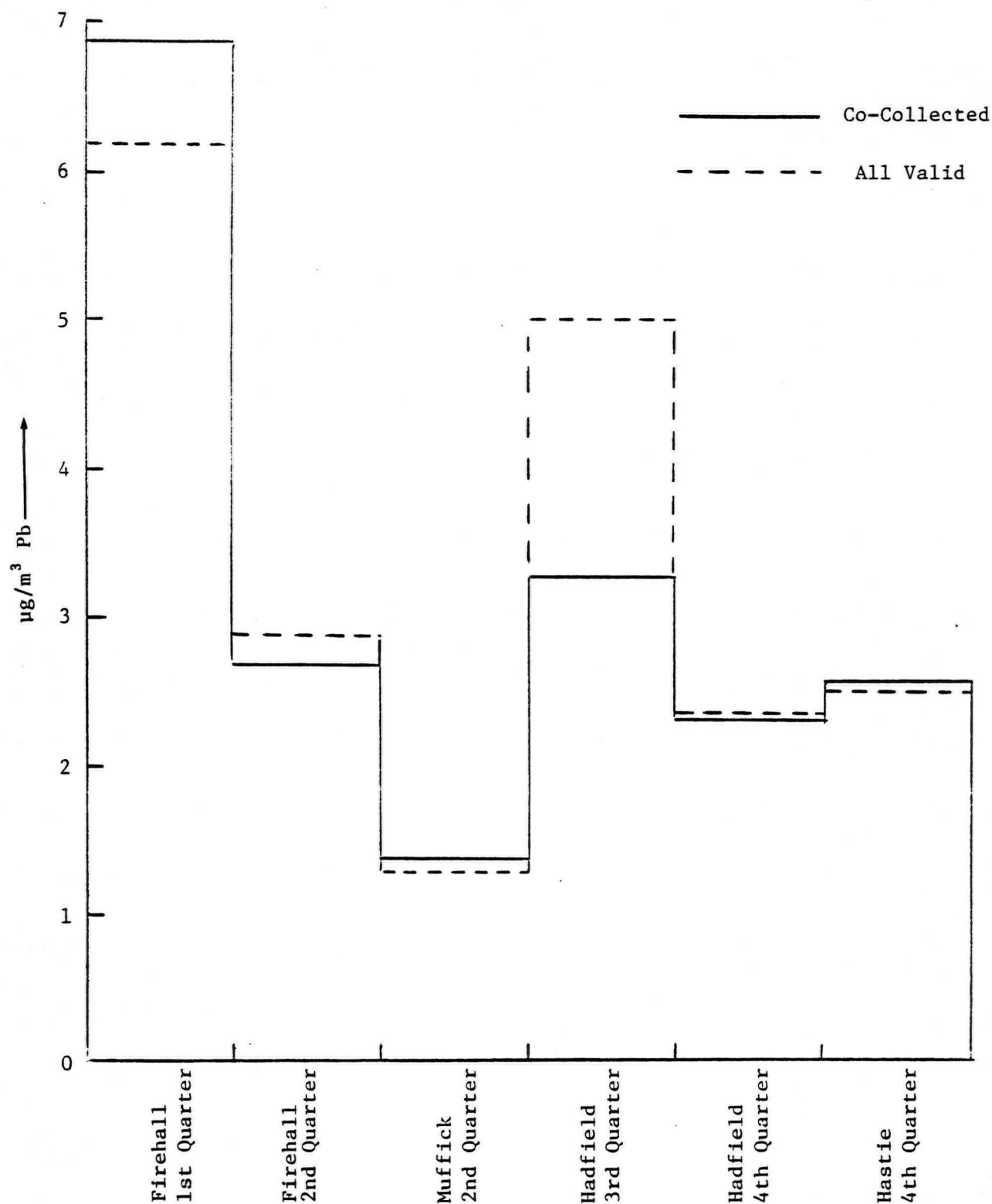


Figure 13 COMPARISON OF MEAN QUARTERLY Pb VALUES DETERMINED FOR ALL VALID HI-VOLUME SAMPLES VERSUS MEAN VALUES DETERMINED FROM THE SUBSET OF HI-VOLUME SAMPLES COLLECTED SIMULTANEOUSLY WITH LOW-VOLUME AND DICHOTOMOUS SAMPLES.

at the Hadfield site rather than all valid samples will be to slightly undercalculate the industrial contribution in $\mu\text{g}/\text{m}^3$ since the lead to TSP ratio of the all valid hi-vol sample means is slightly higher than that of the co-collected means ($4.99/117 = .042$ versus $3.28/84 = .039$).

In addition to the extensive inorganic analyses which were necessary for multielement CMB source apportionment, carbon analyses were performed on five TSP filters (3 lo-vol and 2 hi-vol) to illustrate the relatively high carbon (and total organic) content of ambient aerosols in the East Helena airshed. Table 32 lists the results of the carbon analyses. Elemental, organic and carbonate carbon were measured. The organic carbon content was multiplied by a factor of 1.65 to estimate the total organic content. The 1.65 factor estimates the mass of hydrogen, nitrogen and oxygen associated with carbon in typical natural organic compounds. The contribution of total carbon species (elemental C + organic compounds + CO_3^{2-}) ranged from approximately 15% to 30% in the three samples collected in the spring to around 50% in two samples collected during the winter.

From an overall review of the ambient aerosol analytical results, it is clear that three classes of particles dominate the mass of the aerosols in the East Helena airshed. These are: (1) carbonaceous, (2) metallurgical and (3) geological. The combined impact of metallurgical and geological sources produces an ambient aerosol with an unusually high number of elements at relatively high concentration levels. This complex and exceptionally high elemental composition provides an ambient aerosol well suited for multielement statistical techniques such as CMB source apportionment.

3.2 The Source Data Set

The source data set used in this study consisted of some 79 source fingerprints for each size category, many of which are composites of a number of additional individual source samples. The same 28 elements measured and reported for the ambient samples were compiled in the source

Table 32
CARBON CONTENT - TSP SAMPLES

Site	Date	Sample Type ¹	Organic Compounds ² ($\mu\text{g}/\text{m}^3$)	Elemental Carbon ($\mu\text{g}/\text{m}^3$)	CO_3^{2-} ($\mu\text{g}/\text{m}^3$)	Σ Carbon Species ($\mu\text{g}/\text{m}^3$)	Total Mass ($\mu\text{g}/\text{m}^3$)	Percent Carbon Species
Highway	03/03-09/82	LV	6.2	2.3	0.8	9.3	63.3	14.7
Highway	03/04-09/82	LV	8.0	2.1	0.9	11.0	61.6	17.8
Hadfield	03/11-15/82	LV	15.6	1.3	1.3	18.2	63.0	28.9
Hadfield	11/21/81	HV	24.0	4.2	1.8	30.0	61.0	49.2
Hastie	12/18/81	HV	34.2	10.7	0.4	45.3	85.0	53.3

1. LV = Low-Volume Samples
HV = High-Volume Samples

2. Organic Compounds ($\mu\text{g}/\text{m}^3$) = Organic Carbon ($\mu\text{g}/\text{m}^3$) x 1.65

matrix for comparability in the subsequent CMB modelling. Appendices E, F and G contain the complete listing of the source elemental compositions used for the fine, coarse and total size fractions, respectively. Two sources from NEA's source library (transportation or vehicular exhaust and residual oil combustion) did not have data for the full compliment of 28 elements; however, the elements for which no data were available can be assumed to be at such low concentrations that the implicit assignment of a zero concentration level for them will produce no serious artifacts. Similarly, secondary sulfate $((\text{NH}_4)_2 \text{SO}_4)$ by definition had only one fitting element, i.e., sulfur, since ammonium was not quantified in this study. The third and fourth columns in Appendices E, F and G contain the weight fraction plus or minus the uncertainty associated with each element. The fifth column lists the elemental symbol. The last few columns on the printouts identify the source either by a self-evident description or by codes which can be located in the source tables (Tables 8, 9, 10, 13 and 15) in Section 2.2.

The source matrix can be divided into five classes of sources.

These are:

- ASARCO point sources (major stacks)
- ASARCO and American Chemet process fugitive sources and minor stacks
- ASARCO and American Chemet passive sources (e.g., storage piles) and fugitive emission due to mechanical resuspension (e.g., the New Deal Building)
- Road and soil dust (geological)
- Miscellaneous and area sources, i.e., residential wood combustion, oil combustion, vehicular exhaust and secondary sulfate formation

Sources from each of the categories have been identified as impacting the ambient monitoring sites. Road and soil dust was evident at all sites. Vehicular exhaust and residential wood combustion impacted the ambient aerosol on many of the sampling dates. Industrial fugitive sources were most significant at near-plant sites whereas the impact of ASARCO point sources was more noticeable at sites a greater distance from the plant (the Vollmer, Microwave and Reservoir sites).

Logarithmic plots of elemental concentrations in weight percent are presented in Figure 14 for the three major ASARCO stacks. It was determined during the collection of stack samples that the major fraction of the mass of particles emitted from the stacks was in particles with aerodynamic diameters of less than 2.5 microns. Little difference was seen between the elemental composition between the $<2.5\mu$ and $>2.5\mu$ size fractions collected with the dilution sampling system, consequently the elemental composition of the $<2.5\mu$ was used to represent the elemental composition of the total particulate emissions from the stacks. Significant differences in the chemical fingerprints between the three stacks are apparent. For example, the particles from the baghouse stack contain cadmium at 23% by weight, whereas the main sinter stack particles contain 1.3% by weight cadmium and the zinc stack particles contain 0.078% by weight cadmium. Similarly, the zinc stack particles contain 55% by weight zinc in contrast to 4.5% and 15% for the particles originating from the main stack and baghouse stack, respectively. Major differences in Pb, S and Fe among the fingerprints, as well as many minor differences, permit the three stack sources to be easily distinguishable in CMB modelling. Figure 15 illustrates the chemical fingerprints of baghouse dust samples. A bulk sample of the baghouse stack baghouse dust and a bulk sample of the zinc stack baghouse dust were collected, resuspended in the laboratory and analyzed. A dichotomous and 10-vol sampler also collected a sample of the zinc baghouse dust within the zinc baghouse. As can be seen by comparing Figures 14 and 15, the baghouse dust samples for the zinc and baghouse stacks revealed chemical fingerprints similar to the direct stack samples collected with the dilution sampling system and provide additional confirmation to the chemical fingerprints assigned to those two stacks.

A number of chemical fingerprints are illustrated in Figures 16-18 for process fugitive emissions and minor stacks. Three particulate sources (Figure 16) which have easily traceable fingerprints and have been identified in ambient aerosols in the near-plant East Helena ambient samples are: (1) blast furnace upsets, (2) dross building fugitive emissions and (3) American Chemet's copper kiln stack. The blast furnace upset has a high

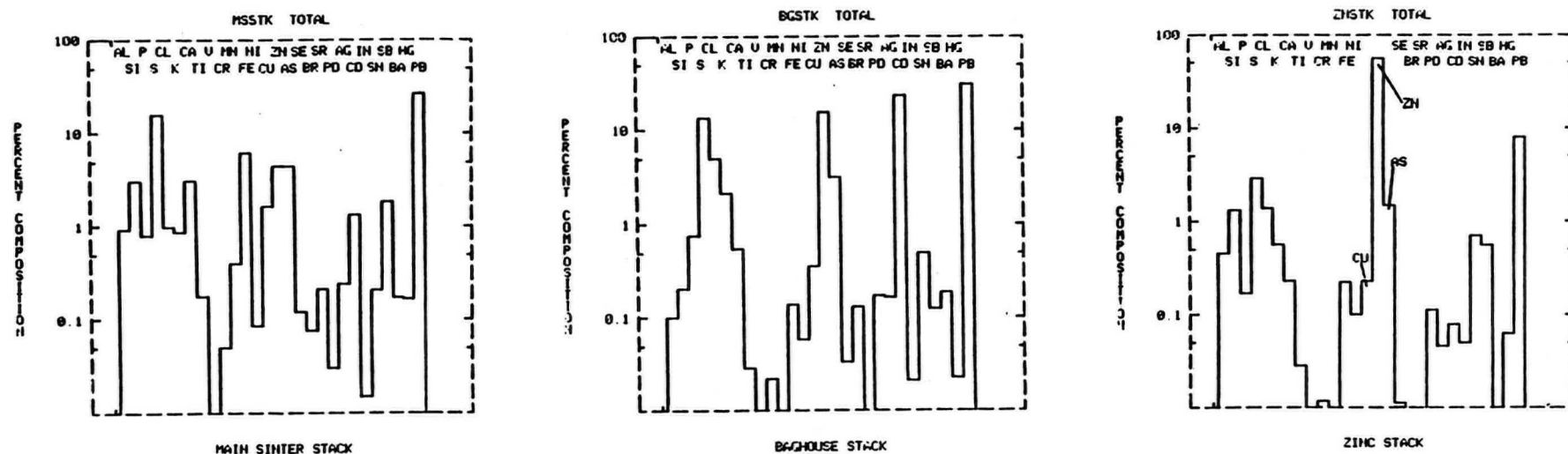


Figure 14. Chemical Fingerprints - ASARCO Point Sources

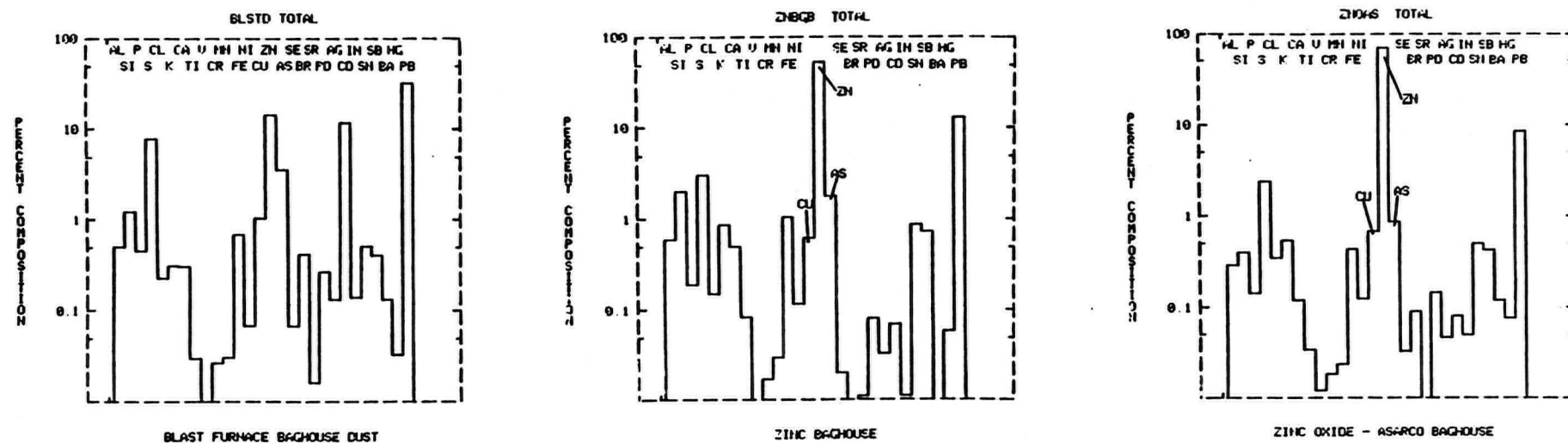


Figure 15 Chemical Fingerprints - Baghouse Samples

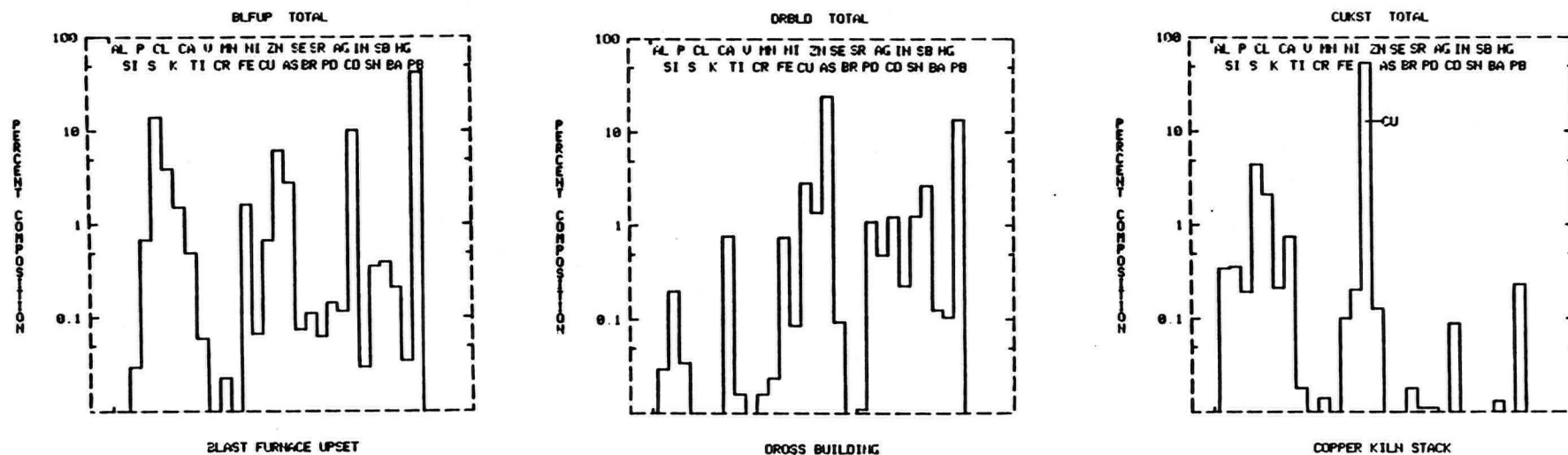


Figure 16 Chemical Fingerprints - Blast Furnace Upset, Dross Building and Copper Kiln Stack

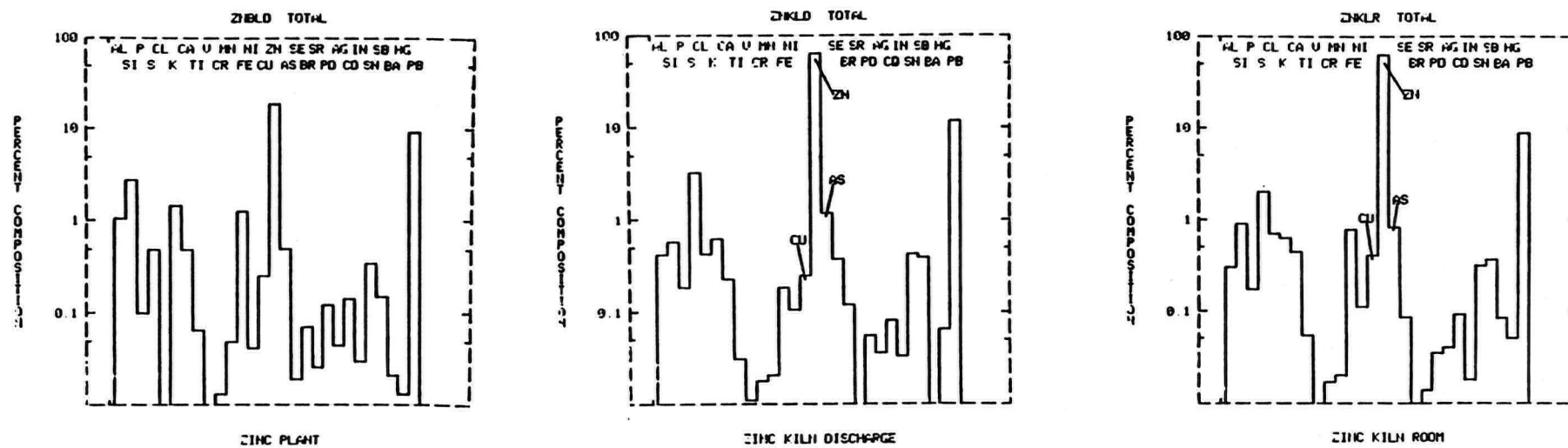


Figure 17 Chemical Fingerprints - Selected Sources of Zinc Oxide Material

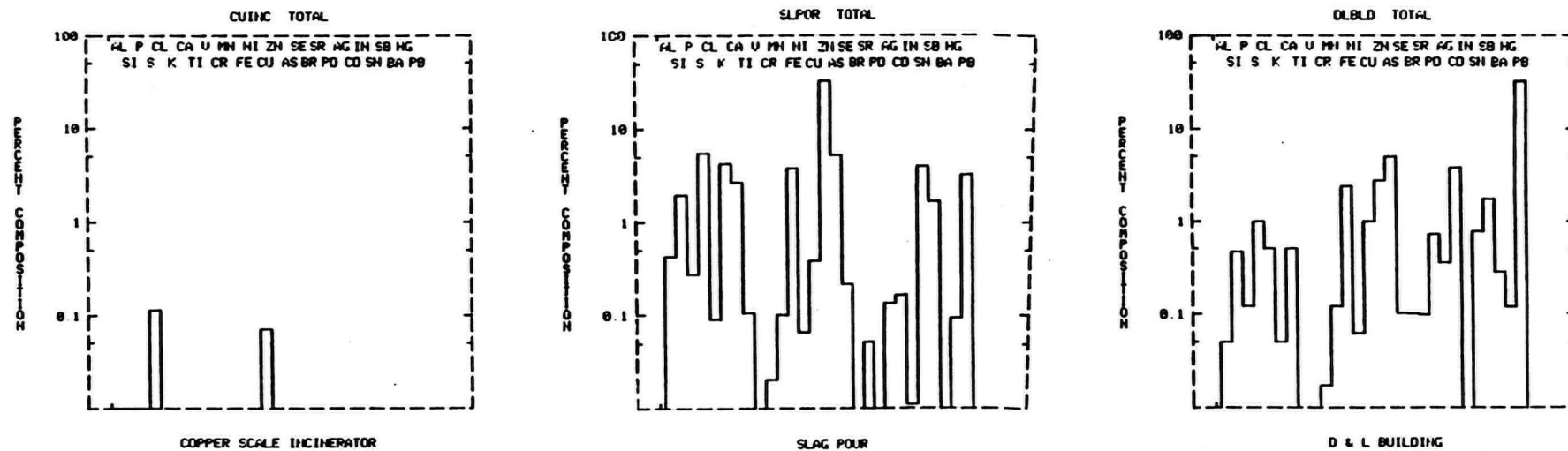
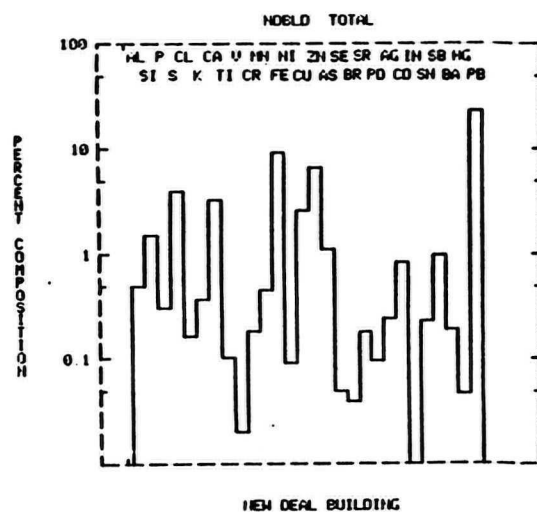


Figure 18 Chemical Fingerprints - Slag Pouring, D & L Building and Copper Scale Incinerator

cadmium and lead content, 10.2% and 42.7%, respectively. The dross building has a high arsenic content and a modestly high lead value, 24.0% and 13.4, respectively. The copper kiln stack produces particles made up of almost entirely a mixture of elemental Cu, CuO and Cu₂O as determined by x-ray diffraction measurements.¹² X-ray fluorescence analysis revealed that the total copper content is 54% by weight. There is also about 0.2% of Ni by weight in the particles. While this is not a high concentration in an absolute sense, it is one of the highest nickel contents seen among the sources measured (except for speiss) and it was a useful feature when the copper kiln was fit by the CMB model. The only source with a fingerprint similar to the blast furnace upset with its high cadmium content was understandably the baghouse stack. The high (and pure) copper content of copper kiln stack and the high arsenic content produced by the dross building made them quite distinct, although the dross building emissions had some copper (2.9%) and speiss from the speiss pit (sporadic stack emissions) had a high copper content (38%) and a moderately high arsenic content (6.5%).

Figure 17 illustrates the chemical fingerprints of zinc oxide material from several sources. These fingerprints were formed from the analyses of (1) a sample collected with a lo-vol sampler at the point of discharge of American Chemet's zinc kiln, (2) samples collected with lo-vol and dichotomous samplers in American Chemet's zinc kiln room near a ventilation opening and (3) samples collected with lo-vol and dichotomous samplers near upper level ventilation windows in ASARCO's zinc furnace building. The chemical character of the zinc kiln room and zinc kiln discharge samples are quite similar and are also similar to the fingerprints of the two samples collected at ASARCO's zinc baghouse (Figure 15), the zinc stack sample (Figure 14) and the fingerprint produced by the resuspension of a bulk sample of American Chemet's zinc fume product (Figure 19). For the aforementioned six samples the key features are (1) a zinc content ranging from 55 to 72% (the zinc stack had the lowest value probably due to dilution by condensible species, (2) a lead content between 8 and 13% (again the zinc stack had the lowest value) and (3) a sulfur content between 2.2 and 3.3%. The samples collected at ASARCO's zinc furnace building had a lower zinc



FUGATIVE EMISSIONS FROM ORE CONC. AND RESID. STORAGE
AND HANDLING.

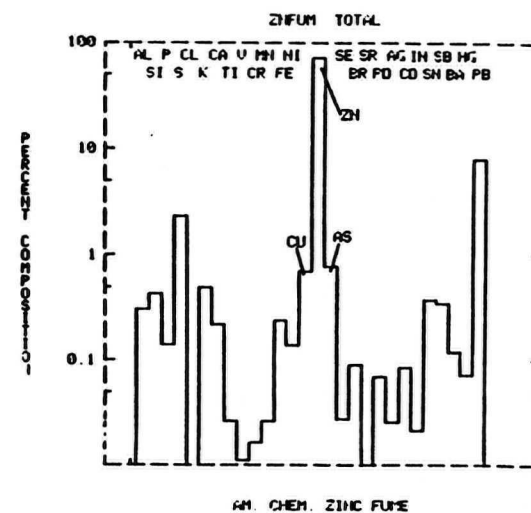
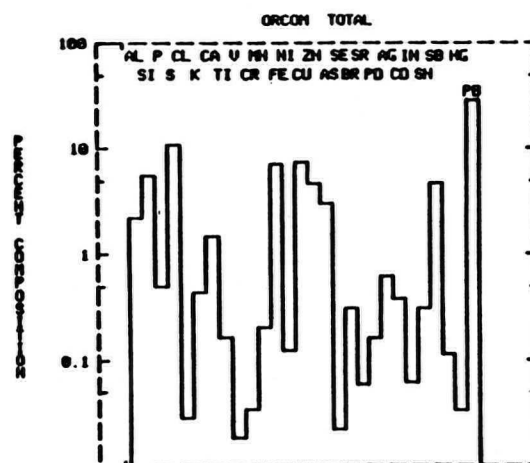


Figure 19 Chemical Fingerprints - Fugitive Dust: Ore Concentrates and Residues and Zinc Oxide Material

content than the pure zinc oxide materials and a slightly elevated concentration of geological elements (viz, Al, Si, Mn and Fe). This is probably due to the mixing effect of pulverized coal (see Figure 20) with the zinc oxide fume. The explosion at the zinc plant where the sampler was employed approximately one week after sample collection due to the ignition of a pulverized coal aerosol further suggests that the small geological component in the zinc plant fugitive aerosol is due to coal.

Figure 18 illustrates the chemical fingerprints of three miscellaneous process fugitive sources. The slag pouring chemical fingerprint can in some ways be qualitatively described as being in between that shown by zinc oxide material and that shown by slag (Figure 20) with the exception that moderately high tin, antimony and sulfur concentrations were measured (3.8%, 1.6% and 5.5%, respectively). The zinc content of the slag pour emissions is lower than that of the zinc oxide material and higher than seen in slag. On the other hand, the iron and silicon content of the slag pour emissions are lower than that of the slag and higher than that of the zinc oxide material. The enrichment in Sn, Sb and S is probably due to the volatile compounds these elements can form. The process fugitive emissions from the D&L building (Sinter building) have a high lead content (23%) and Si, S, Ca, Fe, Cu, Zn and As at the one to ten percent level. The D&L building had a unique fingerprint although without any key marker elements as As is for the dross building or as Cd is for emissions associated with blast furnace. The emissions from American Chemet's copper scale incinerator were almost entirely organic with only Cu and S detectable at around the tenth of a percent level. The copper scale incinerator samples had an oily organic appearance.

Figures 19 and 20 illustrate the chemical fingerprints of some important fugitive dust sources. Because many different types of ore concentrates, residues and related materials are stored and handled on the ASARCO plant complex (Table 33), two methods were used to construct a representative source fingerprint of the overall fugitive dust from the storage and handling of these materials. First, dichotomous and 10-vol

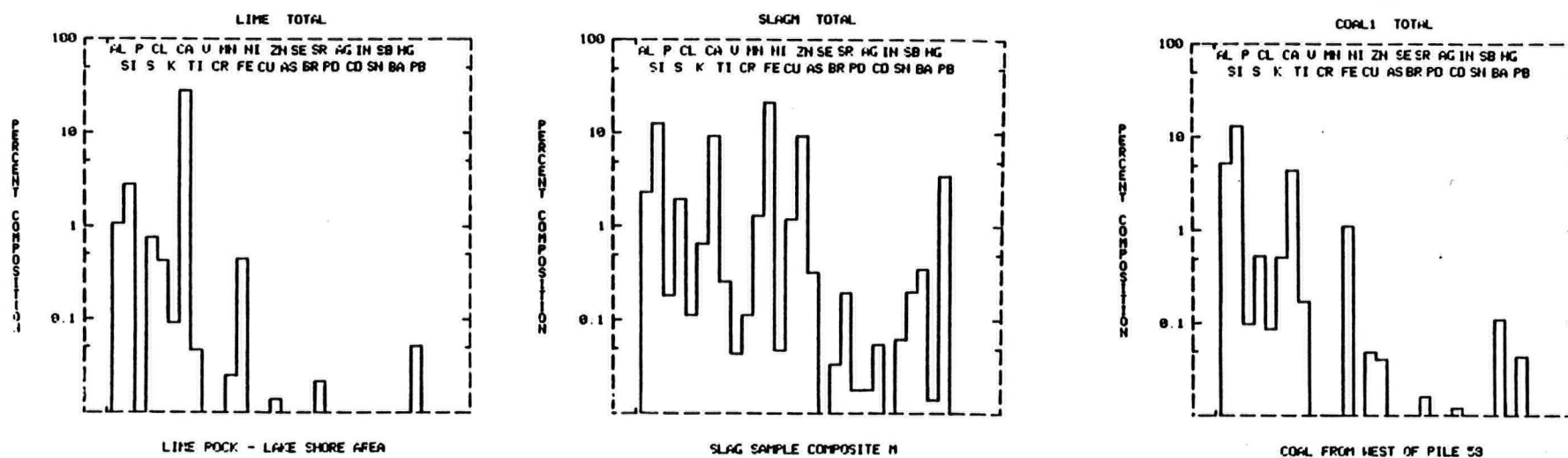


Figure 20. Chemical Fingerprints - Fugitive Dust: Lime Rock, Slag and Coal

Table 33

Material Storage Piles - ASARCO Plant, November 1, 1981

#	tons	#	tons	#	tons
1 Blackwell Coal	44	730 Crystal	337	868 TGS	No Wt.
51 Hiawatha Coal	1570	738 Misc'l. Cds.	442	869 Elaytoy Silver	No Wt.
52 Bear Coal	1452	739 Sherwin Williams Res.	89	870 Grande	No Wt.
53 Hiawatha Coal	183	740 Brooklyn	42	871 Mohawk	No Wt.
54 Bear Coal	94	742 Omaha Skims	94	872 Tacoma	No Wt.
56 Bear Coal	open	750 Julcani (TrkWt.)			
58 Loma Coal	open	753 Galena	86		
60 Petro Coke	386	756 Tacoma Dust	226	963 Anaconda Res.	643
61 Ferme Coke	open	762 Indio (TrkWt.)		973 Ecstall Res.	47
62 Ferme Coke		782 Glover	292	1057 Castro	707
63 Ferme Coke	133	784 Galena	104	1060 Castro	610
64 Alabama Coke	open	787 RR # 2	692	1062 Castro	578
70 Michel Breeze	open	791 Tacoma Dust	87	1110 Castro	498
75 Petro Breeze	217	794 SS Py/TGS	467		
		798 MT Isa	170		
		799 MT Isa	169		
		800 MT Isa	190		
		801 MT Isa	184		
		802 MT Isa	55		
		805 Glover Dross	186		
		809 Pyramid	2		
279 Omaha Skims	85	811 Mix Residue	4706		
302 Precious Mets (Trwt)		812 Buick	290		
305 X-ray Ash (Mill) 418 lbs.		813 Tacoma Dust	72		
314 Sel Rex	No Wt.	814 Misc'l. Dusts	438		
315 Sel Rex	No Wt.	817 Misc'l. Cds.	647		
316 Sel Rex	No Wt.	837 Big Buffalo	735 lbs.		
317 Sel Rex	No Wt.	840 Consolidated Ag	94		
318 Sel Rex	No Wt.	841 Misc'l. Dusts	175		
319 Sel Rex	No Wt.	843 Glover Dross	190		
320 Sel Rex	No Wt.	846 Ecstall Res.	427		
321 Homestake Carbon	No Wt.	847 Rumley	1422		
322 Echo Bay	No Wt.	848 Keno (TrkWt.)			
323 X-ray Silver 15,210 ozs.		849 Mix Res.	446		
324 Yellowknife		850 Castro	692		
Carbon 15,210 ozs.		851 Glover Dross	196		
325 Echo Bay 15,210 ozs.		852 TGS	565		
326 Eldorado 15,210 ozs.		853 Galena	92		
		854 Mix Res.	1068		
		855 Buick	385		
		856 Misc'l. Cts.	84		
		857 Tacoma Dust	171		
427 Glover Dross	281	858 Guiruvilea	197		
522 Castro	607	859 Guiruvilea	592		
524 Castro	691	860 Plaza	No Wt.		
592 Omaha Dust	163	861 Plaza	No Wt.		
669 Brooklyn	190	862 Serap. Glass	22		
703 Castro	198	863 Alianza	589		
705 Castro	666	864 Castro	99		
706 Castro	630	865 Alianza	195		
713 Bunker Residue	1146	867 Julcani	No Wt.		

Samples Not Included
On List, Collected 11/3-4

* Lower Storage Area *

File 873

Tan colored material, plant
west of thaw house, not on
concrete pad

Nabob Mill Elp 101

Brazos Concentrate

Klondike for October

File 890

Gray-green ore concentrate

Near RR track

New pile by RR track gray to
black in color

* Lake Shore Storage Area *

File 875

File 891

File 874

File 892

Unknown brown material next to
blast furnace flame

samplers were run in the ore blending and proportioning building (New Deal Building) and second, bulk samples were collected from each of the major storage piles. From data provided by ASARCO, the most important (i.e., most abundant and routinely used) materials were grouped together by origin to form composites samples (Table 15, Section 2.2). The fingerprints of each of the fourteen composites formed (O-A through O-N) are listed in the source appendices. To provide an overall composite fingerprint the elemental data for each of the fourteen composites were mathematically averaged to form a weighed mean composite which is referred to as ORCOM in Figure 19 and in the source Appendices. The mean was weighed in such a fashion to represent correctly the number of individual piles of each material (a crude abundance weighing). The key features of the two samples which were used to represent fugitive emissions from ore concentrations and residues were: (1) a high lead content (23% for the New Deal Building sample and 29% for the ORCOM fingerprint), (2) geological elements (Al, Si, Ca) at or near the percent level and (3) mineralogical elements (S, Fe, Cu, Zn, As and Sb) from the one to ten percent level. The fingerprints compiled for the New Deal Building sample and for the ORCOM sample compare remarkably well. The uncertainties associated with the ORCOM samples are, however, much larger than those associated with the New Deal Building sample since the latter are analytical uncertainties and the former are standard deviations obtained when the 14 ore composite fingerprints were averaged. A zinc oxide fingerprint is also included in Figure 19 since the handling of zinc oxide by ASARCO and American Chemet is a possible fugitive source of particles. The chemical composition of the zinc oxide fugitive dust, is of course, similar to the other zinc oxide samples previously discussed.

Figure 20 illustrates the chemical composition of three fugitive dust sources. Lime rock (limestone) is, as would be expected, dominated by calcium and to a lesser extent other geological elements. Sources of particulate limestone include (1) resuspension of dust off haul trucks which regularly run between the ASARCO plant and the quarry near Montana City, (2) resuspension of road dust along the haul route which has been found to be highly enriched in calcium due to its long history of use, (3) windblown dust off the large lime rock pile at the "Lake Shore" storage area, and (4) resuspension due to handling the lime rock on the plant complex.

The first two possible sources are highly visible. Because the limestone composition of natural soils varies significantly over a short distance in the soils in the East Helena area, some of the limestone which shows up in the CMB fits may be due to not characterizing the soil chemistry of all the soil particles which impact a given site precisely enough. For example, if more than one soil or road dust type impacts a receptor and the type which has the major impact is low in CaCO_3 , whereas one type which has a high CaCO_3 component has a low impact, the best CMB fit using the major soil or road dust fingerprint will also require the lime rock source as well to make up for the small CaCO_3 deficiency.

Four composite slag fingerprints have been compiled. The one representing the slag mining area is illustrated in Figure 20. The slag mining area due to the active mining with heavy equipment is the most likely (major) source of slag particles. The slag chemical compositions are dominated by Zn, Fe, Ca and Si. Lead varied from 3 to 9% in the slag samples.

The fingerprint of a coal sample is also illustrated in Figure 20. Seven coal and coke samples were collected at various points on and near the ASARCO plant. Coal and coke are primarily organic with their inorganic composition geological in nature (i.e., Al, Si, K, Ti, Cu, Fe) plus having a moderate and variable sulfur content. Numerous transition and heavy metals also appear at the trace level in the fingerprints depending on the sample's origin. Windblown dust from storage piles, resuspended dust from material handling and the coal pulverizing plant discharge are all possible sources of coal and/or coke particles. The coal pulverizing discharge was observed to produce a plume of high opacity and quickly loaded filters on samplers located in its path.

Nineteen composite road dust and soil samples were analyzed and are listed in the source Appendices. The key features of the road and soil dust samples are (1) high Al, Si, K, Ca and Fe concentrations with the Ca content being variable depending on the limestone content, (2) intermediate concentrations of Ti and Mn and (3) low to high concentrations of

anthropogenic elements (viz, S, Cu, Zn, As and Pb) depending on the sample site's proximity to the ASARCO and American Chemet plants. Lead, for example, ranged from approximately 0.1% in the soil near the Padbury ambient monitoring site to 2.9% in the road dust of Highway 12 to the north of the plants. Similarly, copper ranged from approximately 0.04% in the Padbury soil to 2.7% in the Highway 12 sample. Figure 21 illustrates the chemical fingerprints of the Padbury site soil, of a city street dust sample collected in East Helena and of the Highway 12 sample collected directly north of the plants.

Three easily identifiable combustion sources are illustrated in Figure 22. These are residential wood combustion, residual oil combustion and vehicular exhaust. Even though the particles generated by these sources are primarily composed of organic compounds and elemental carbon, they have inorganic elemental fingerprints which allow them to be identified by CMB modelling. Residual oil has an unusually high V and Ni content. Wood smoke has a high K content and vehicular exhaust has high Pb and Br concentrations. The Helena wood smoke sample which was analyzed was found to have 36.1% organic carbon (an estimate of the total organic compound content would range from 54-72%), 17.5% elemental carbon and a total inorganic content of 6% (not including oxide oxygen). Vehicular exhaust and residential wood smoke combustion were found to regularly impact the East Helena ambient samples.

A secondary sulfate fingerprint was created to account for sulfate formation from gaseous SO_2 . This source was assigned the chemical composition of $(\text{NH}_4)_2\text{SO}_4$ and was used only in the fine fraction ($<2.5\mu$) CMB fits since secondary sulfate particles are known to be primarily in that size fraction. Lead smelting, of course, emits considerable quantities of gaseous SO_2 .

A number of miscellaneous bulk samples were collected but the CMB modelling showed that they did not represent a major impact on any of the ambient samples. These sources included: (1) an ASARCO clean-up pile in

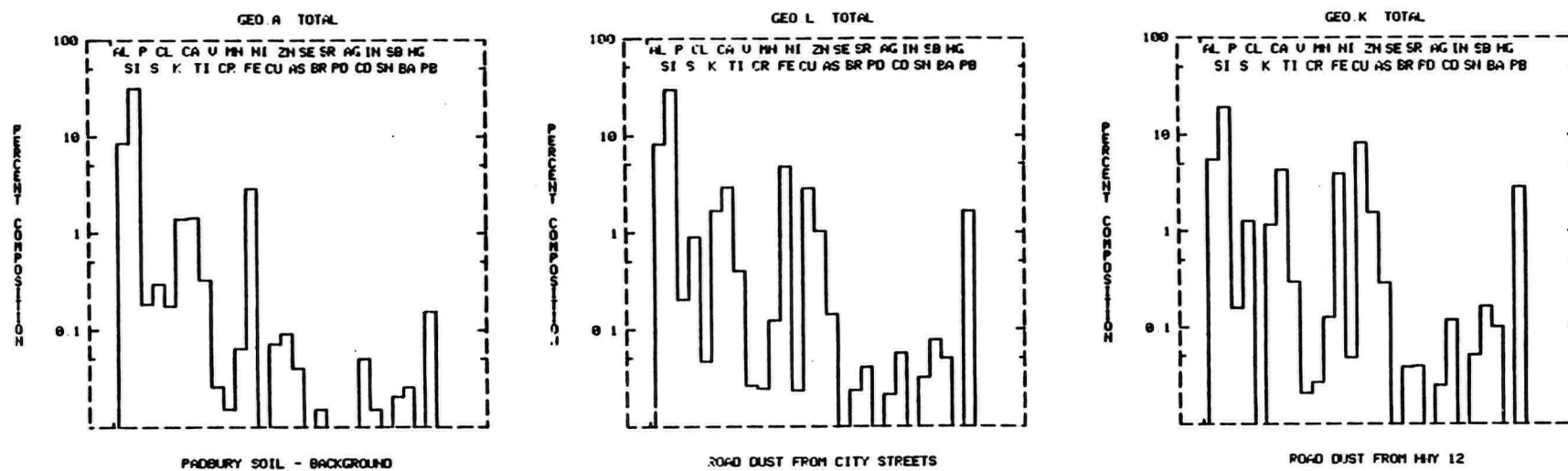
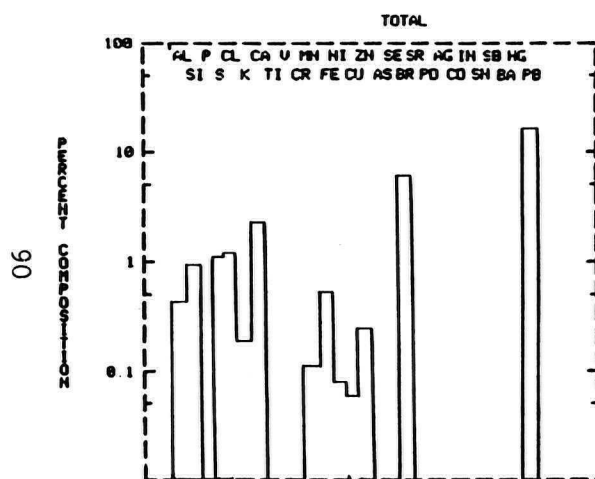
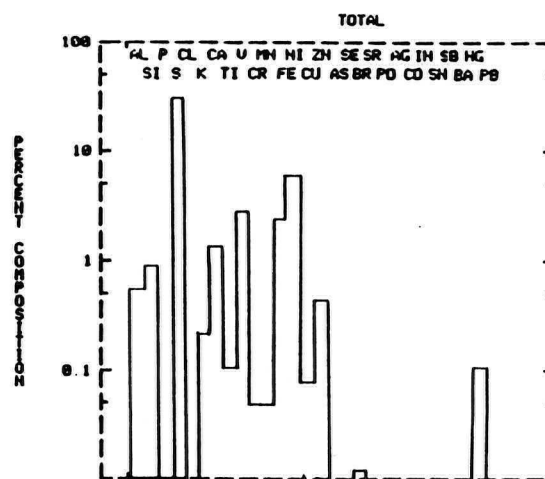


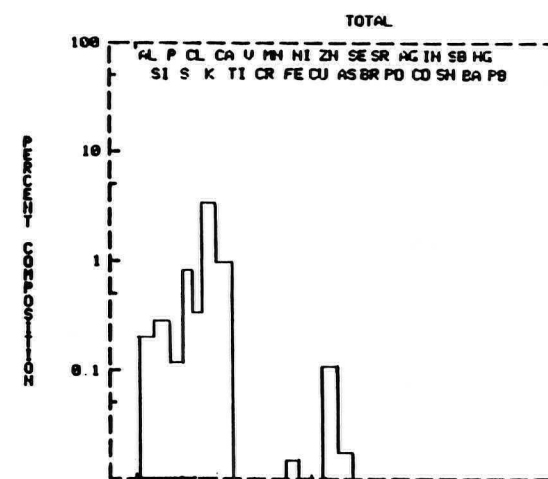
Figure 21. Chemical Fingerprints - Road and Soil Dust



VEHICULAR EXHAUST



RESIDUAL OIL COMBUSTION



RESIDUAL WOOD COMBUSTION

Figure 22. Chemical Fingerprints - Area Combustion Sources

the lower storage area, (2) dross skims, (3) bulk sinter, (4) sulfur flux, (5) soda flux and (6) acid plant hot cottrell and baghouse dust. The chemical fingerprints for these samples as well as several others of low priority are included in the source Appendices (E, F and G).

The East Helena source matrix represents perhaps the most extensive and well defined compilation of source data used in any CMB study to date. Both the number of sources from which samples have been collected and analyzed, and the number of elements which can be quantified due to the metallurgical nature of most of the sources combine to provide more than adequate information for CMB source apportionment.

3.3 CMB Source Apportionment

The CMB source apportionment results are graphically illustrated for the seven key mean quarterly ambient data sets (Table 31) in Figures 23-29. The individual CMB results for mean quarterly data sets for all three size fractions (fine, coarse and lo-vol TSP) at all eleven sites studied during 1981 are compiled in Appendix I and the CMB results for four individual dichotomous sets and three lo-vol samples (multiday samples) collected at the Reservoir site in 1982 are compiled in Appendix L.

Source apportionment for both mass and lead concentrations have been conducted for each of the key mean quarterly data sets and are presented in Figures 23-29. The source contributions to ambient mass (TSP) and lead concentrations vary with site and quarter, however, it is clear which sources are the overall major contributors. The overall major sources of TSP in the East Helena airshed are: (1) road and soil dust, (2) fugitive ore concentrate and residue emissions, (3) carbonaceous sources (residential wood combustion, coal dust, and unexplained H, O, N and C probably from miscellaneous combustion sources, agricultural materials and pollen), (4) a zinc oxide rich material and (5) American Chemet's copper kiln. The overall major sources of lead are: (1) road and soil dust, (2) fugitive ore concentrate and residue emissions, (3) blast furnace upsets and (4) a zinc oxide rich material. The blast furnace upset is a major source of lead even though it is a minor source of TSP due to its high lead content (43%).

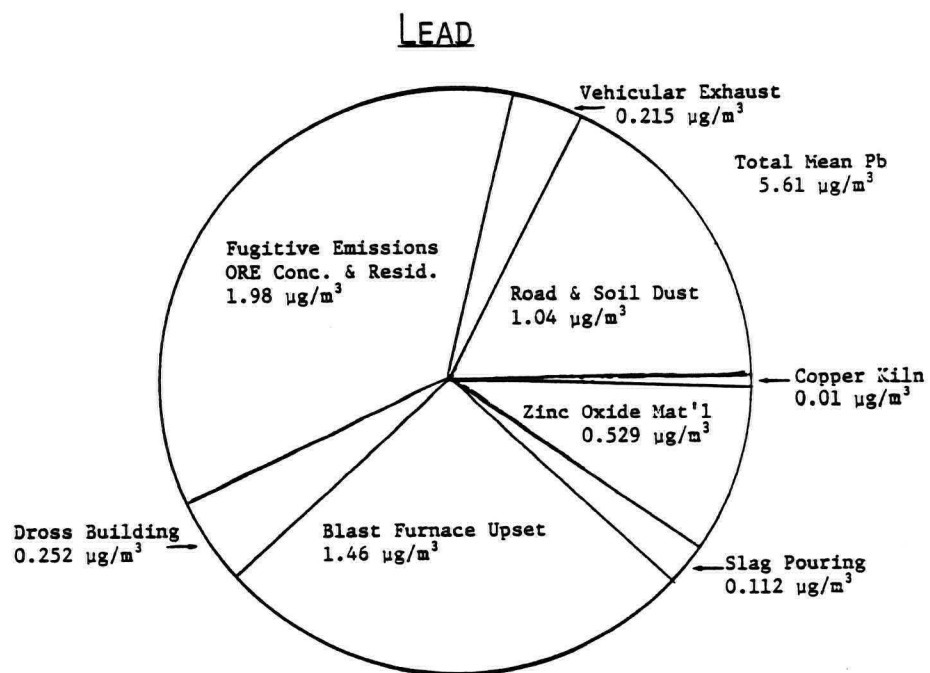
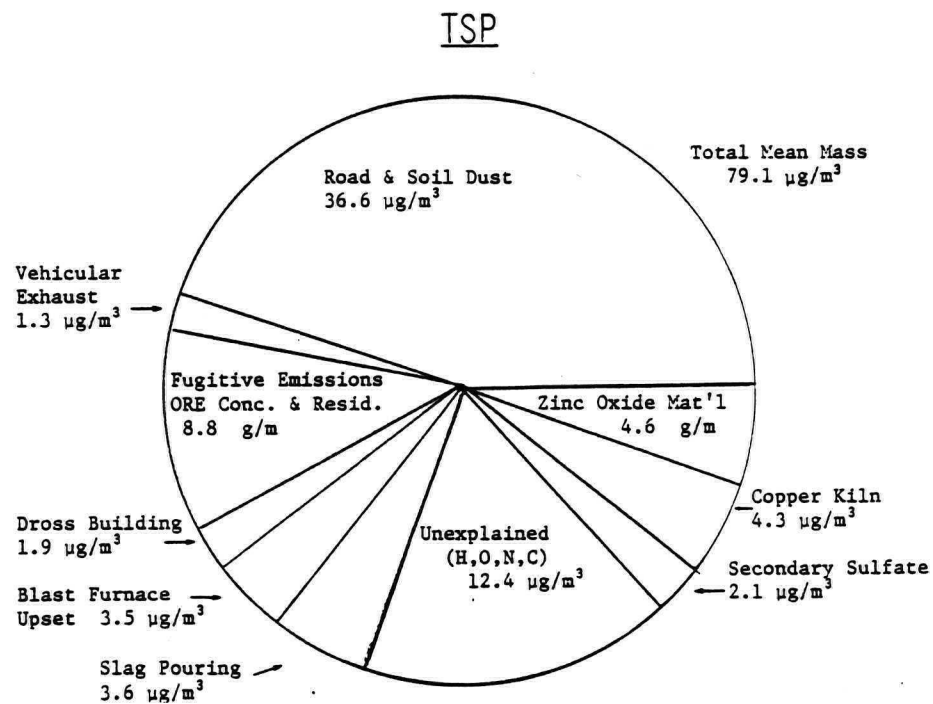


Figure 23. CMB Source Apportionment - Firehall Site, First Quarter

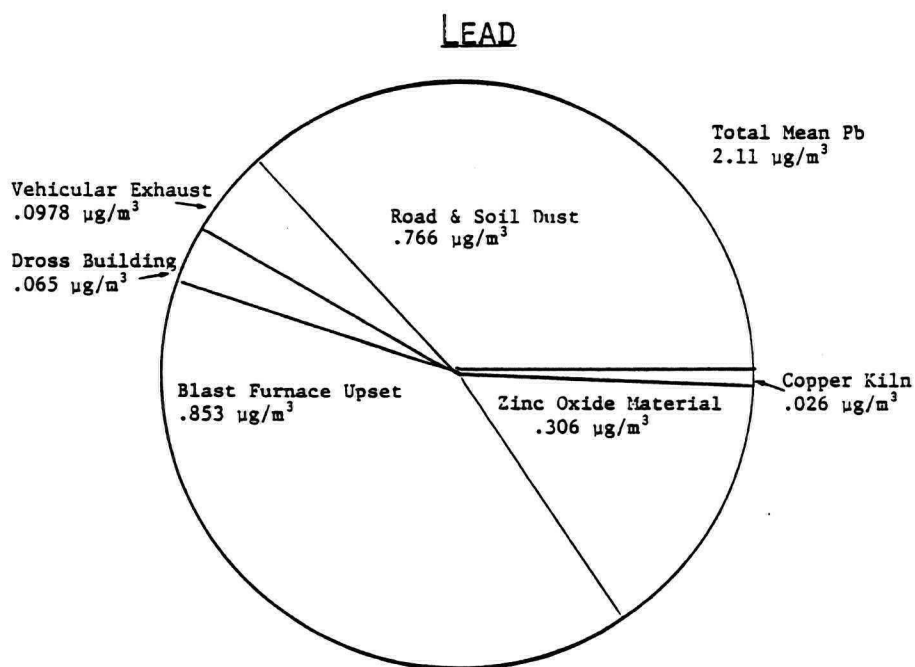
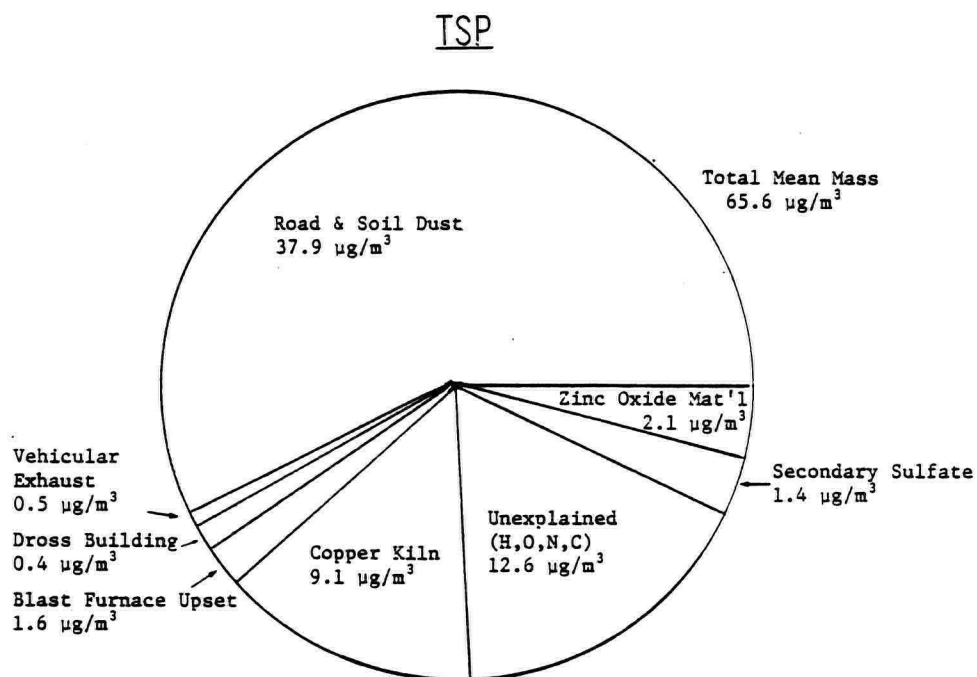


Figure 24. CMB Source Apportionment - Firehall Site, Second Quarter

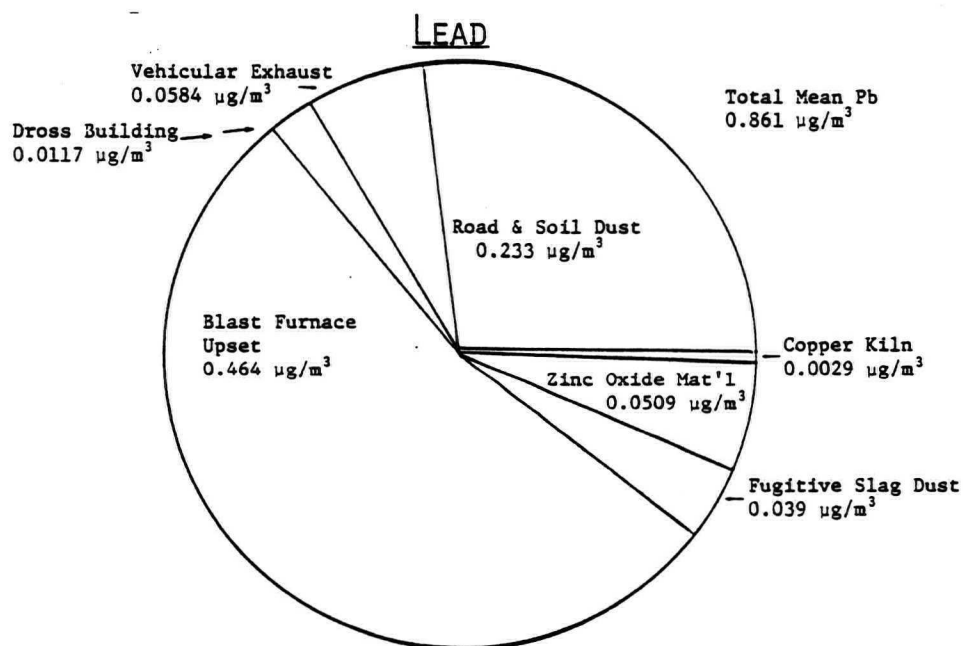
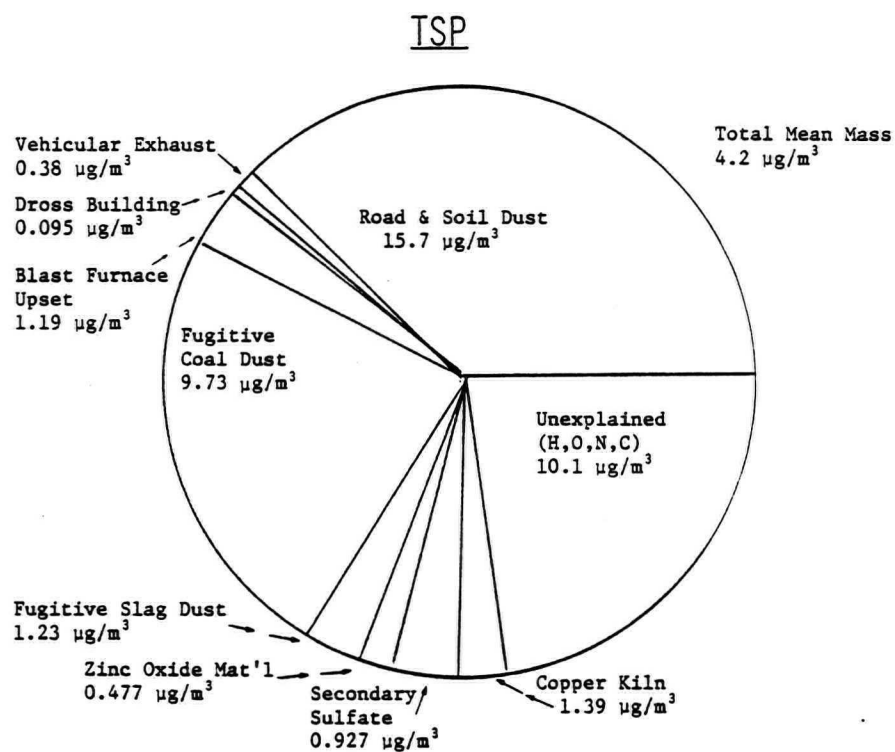


Figure 25. CMB Source Apportionment, Muffick Site, Second Quarter

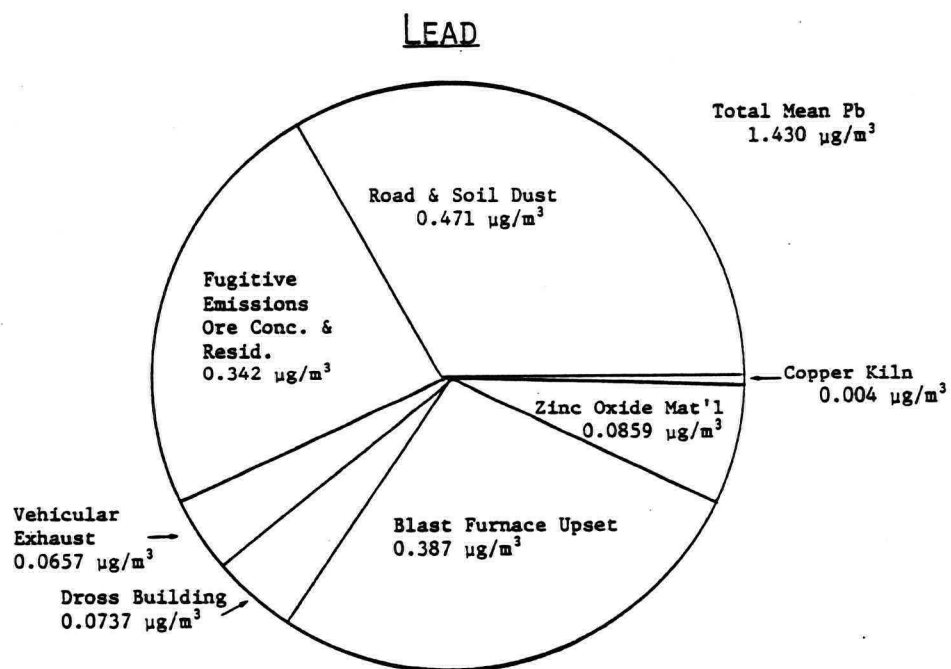
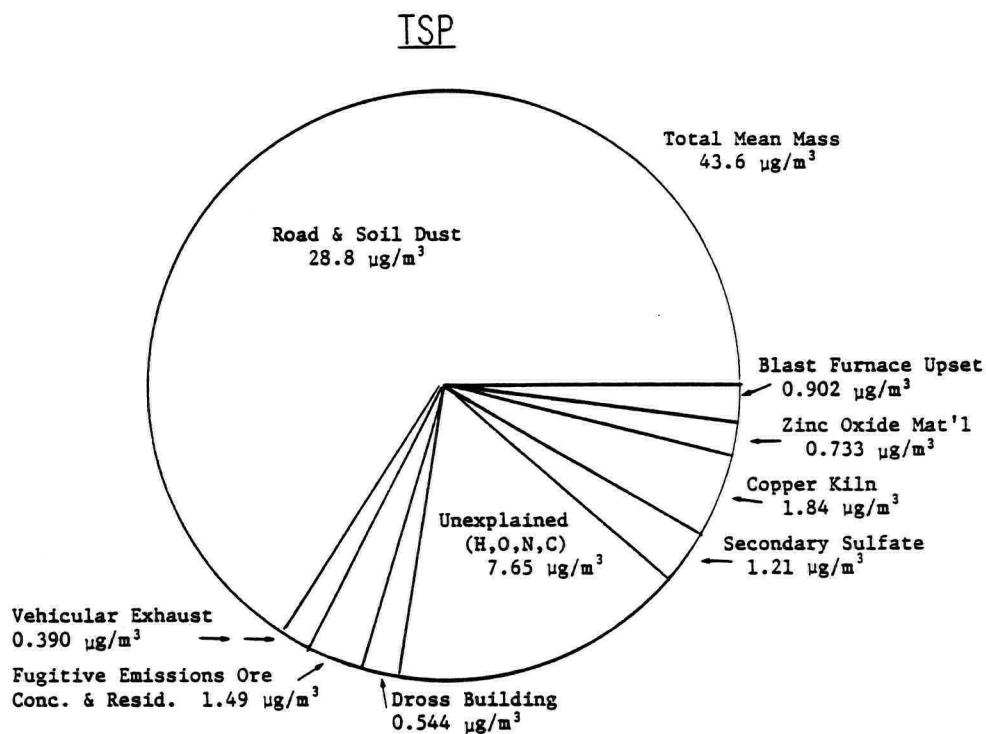


Figure 26. CMB Source Apportionment - Hadfield Site, Third Quarter

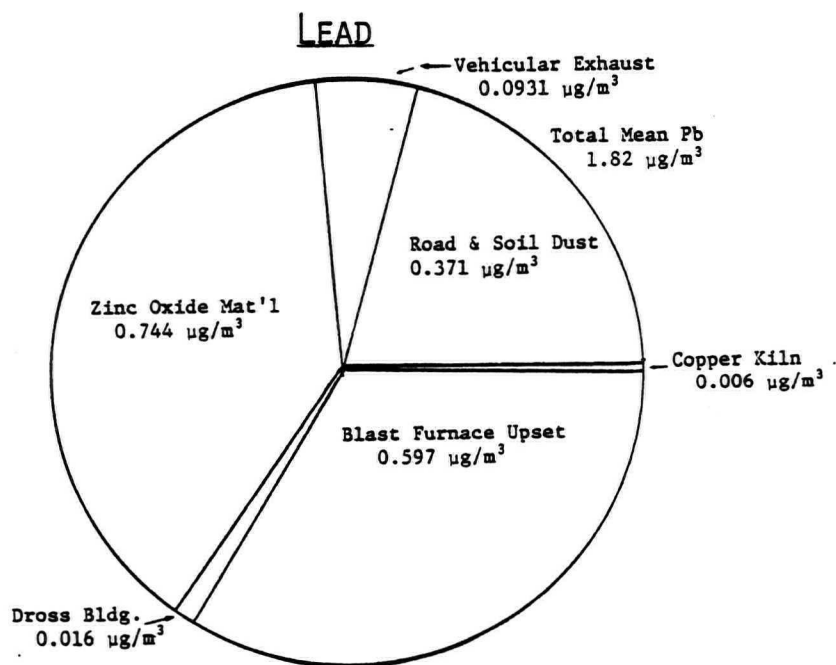
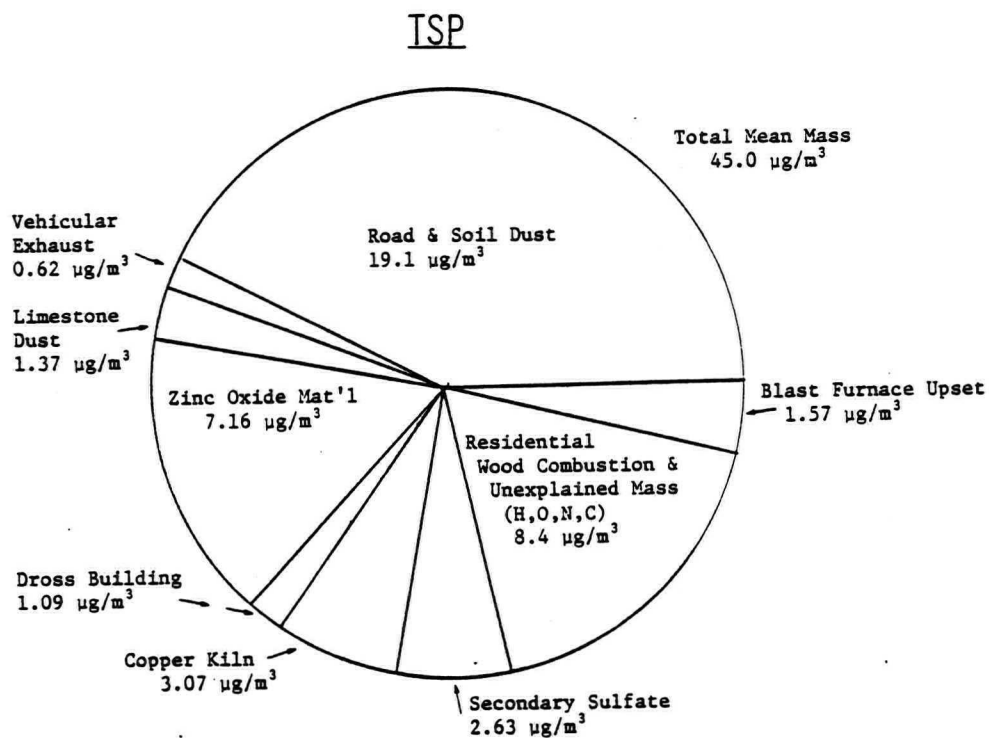


Figure 27. CMB Source Apportionment - Hastie Site, Fourth Quarter

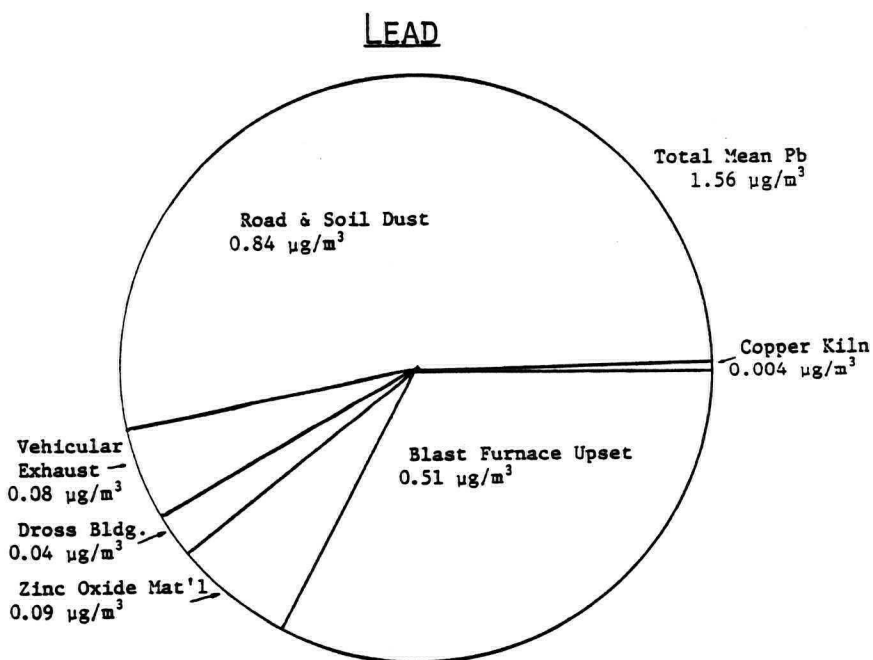
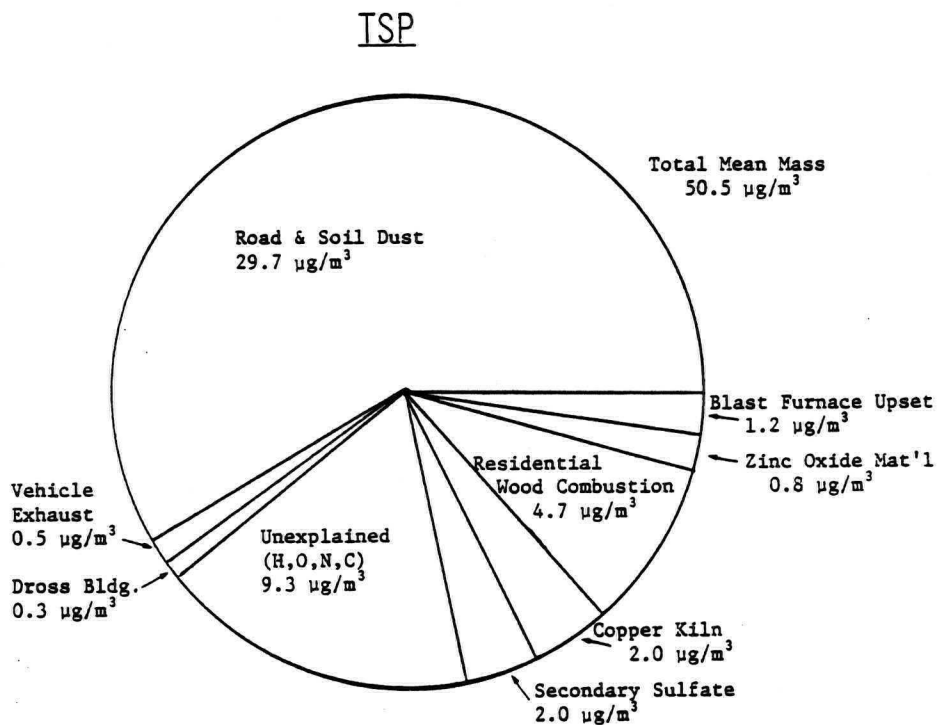


Figure 28. CMB Source Apportionment - Hadfield Site, Fourth Quarter

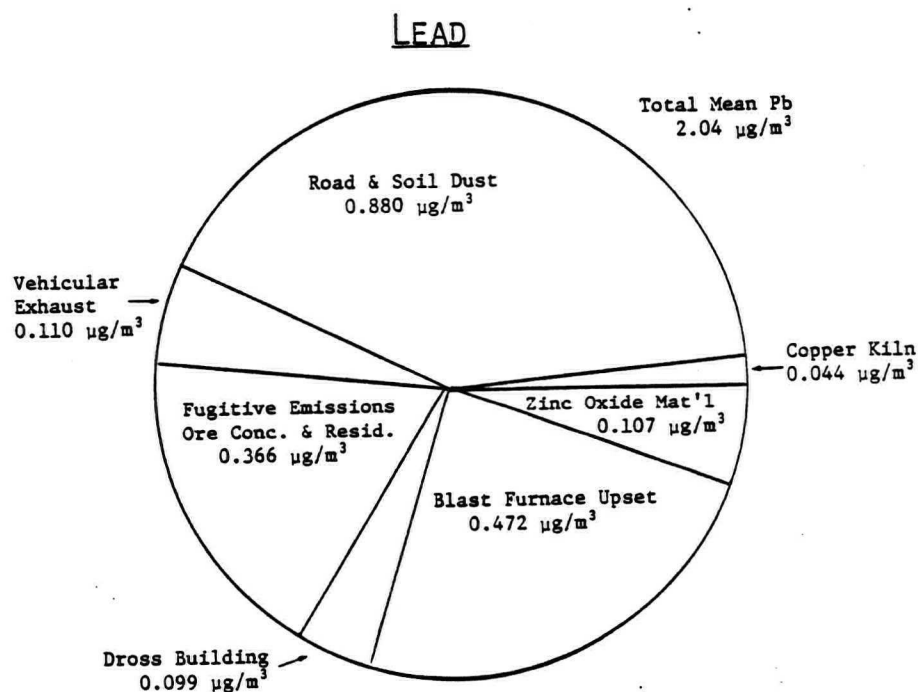
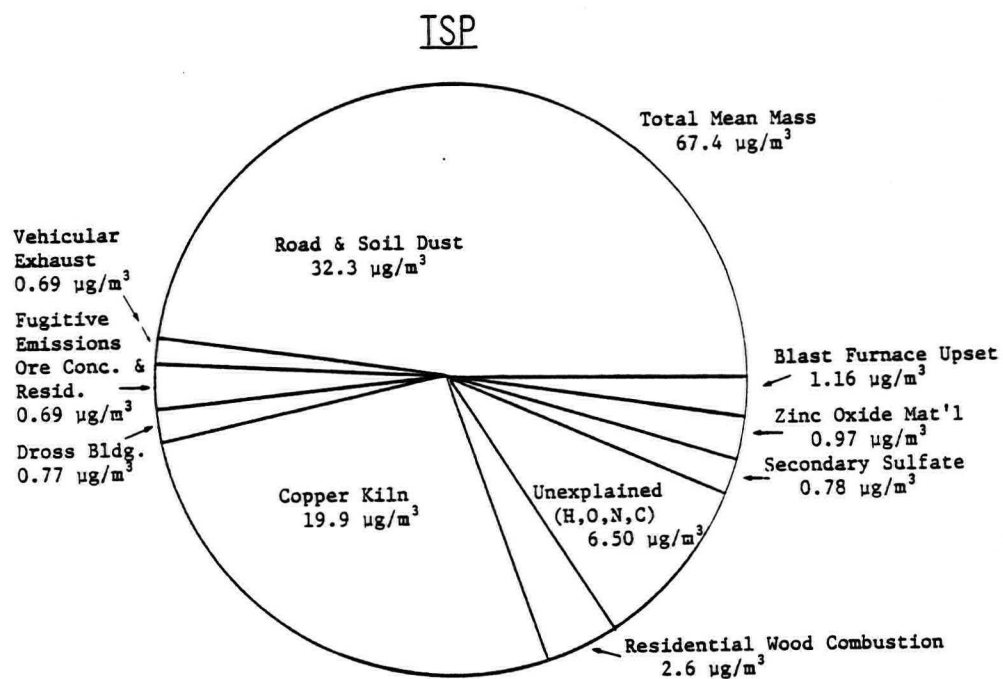


Figure 29. CMB Source Apportionment - Highway Site, Fourth Quarter

American Chemet's copper kiln on the other hand, is often a major (or at least intermediate) contributor to TSP but its contribution to ambient lead concentrations is very small due to its low lead content (0.2%).

Minor TSP sources are: (1) vehicular exhaust, (2) dross building fugitive emissions, (3) blast furnace upsets, (3) slag pouring, (4) secondary sulfate, (5) fugitive slag dust and (5) limestone. Minor but measurable lead sources are: (1) vehicular exhaust, (2) dross building fugitive emissions, (3) slag pouring, (4) fugitive slag dust and (5) American Chemet's copper kiln (very small).

For the road and soil dust source category, it is worth noting that road dust sources provided the best CMB fits for the key mean quarterly data sets illustrated in Figures 23-29. Soil was left in the title, "Road and Soil Dust", because small contributions of soil dust would not be separatable from the larger road dust contribution due to their similar chemical fingerprints. When CMB source apportionment was conducted on individual 24 hour samples during the quarters from which the quarterly means were determined, it was found that in a significant minority of the days soil dust provided a better fit than did road dust. It is also interesting to note that the road dust source fingerprint determined from city streets (composite L) provided the best mean quarterly fit at each of the key sites during the second and third quarters, whereas the road dust source fingerprints for Highway 12 (composites K and Q) provided the best mean quarterly fit during the first and fourth quarters. Again it must be emphasized the CMB source apportionment on quarterly mean values will assign the contribution to the dominate source among sources with very similar chemical compositions and some fine detail is lost, e.g., there was some city street dust impact on the ambient samplers during the first and second quarters and there was some highway dust impact during the second and third quarter.

An attempt was made to identify the sources of pollutants in one of the most contaminated road dusts (composite K) by performing CMB modelling on it as if it were an ambient air sample. Some illustrative

information was obtained from the exercise, however the results must be viewed as semi-qualitative for two reasons: (1) the CMB model requires the chemistry at the receptor to be unaltered, i.e., the chemical composition of the pollutants at the receptor must be the same as it was at the source and (2) that all major sources of pollutants be identified. Due to long term leaching (for example, CdSO_4 is quite water soluble; PbSO_4 is not) and due to contributions from various sources over many decades, neither of the aforementioned two requirements are met with an "ambient" soil sample. The CMB modelling with composite sample K did show that: (1) approximately 54-56% of the mass was pristine soil, (2) 4% of the mass was limestone, (3) 9-14% of the mass was slag, (4) 13 to 14% of the mass was copper kiln material and (5) 5 to 10% was unexplained (a fraction of which is probably organic). Nearly all the lead in the road dust was from industrial activity with the small, typical vehicular exhaust component being "swamped". It should be noted that the purpose of studying the sources of pollutants in road dust and soils is that they can be viewed as an intermediate in industrial air pollution. Control strategies to mitigate such problems as lead non-attainment should include methods of preventing future lead contamination of roads and soils which will eventually be resuspended themselves.

Several other points should be made concerning the CMB modelling and the construction of the source apportionment pie charts (Figures 23-29): (1) The secondary sulfate mass was determined from CMB modelling with the fine fraction quarterly mean values that were co-collected with the lo-vol TSP samples. The mass attributed to secondary sulfate was subtracted from the otherwise unexplained portion of the lo-vol TSP pie chart. Sulfur was not used as a fitting element in either the coarse or lo-vol TSP data due to the sulfate artifact compounds identified by XRD analyses¹² and due to the fact that secondary sulfate is known to be primarily in the fine size fraction. (2) Residential wood combustion and the unexplained mass were grouped together in the Hastie site fourth quarter CMB data. Fitting residential wood combustion to the data greatly improved the quality of the CMB fit in that the reduced chi-square value decreased

markedly and the measured to calculated ratio for most elements improved. However, the total mass predicted from the CMB model was substantially higher than what was actually measured. This same phenomenon was observed when CMB modelling was conducted on many of the individual 24 hour samples and suggests that the inorganic elemental fingerprint which was used is correct (in a relative sense) but may not be representative of the absolute amount of inorganic and organic material under all burning conditions, fuel types, ambient temperatures, etc. (3) A small portion of the blast furnace upset contribution which was calculated may be from the baghouse stack since there is some similarity in their chemical composition (viz, high Cd and Pb), and (4) It is impossible to tell from CMB source apportionment alone which of the zinc oxide sources contributed to the ambient TSP and Pb levels since they all have similar chemical make-ups.

As previously mentioned, the individual CMB results for mean quarterly data sets for all three size fractions, for all eleven primary sites and for both co-collected and all valid samples are compiled in Appendix I. In several cases both a CMB printout with residential wood combustion and one without residential wood combustion were included when wood combustion improved the quality of fits but at the same time overpredicted the mass. The reservoir site at which multiday samples only were collected in spring of 1982 is included in Appendix L. The ambient sampler collected at the reservoir site show a very high limestone component which is not surprising due to the site's proximity to the limestone quarry and to a cement plant. The quality of the fits are, in some cases, not very good at the Reservoir site probably due to the fact that no fingerprints were included for emissions from the cement plant sources.

To aid in understanding the CMB printouts in Appendices I and L, an example printout is presented here (Figure 30). The first five lines provide descriptive information. The first line of the printout gives the filter number on which the sample was collected (HD559). The second line gives the size fraction (coarse). The third line gives the sampling

COARSE PARTICULATE FRACTION

SAMPLING DATE: 820412 SITE CODE: 4

SAMPLING DURATION: 48 HRS.

SITE: HADFIELD

EFFECTIVE VARIANCE FITTING. REDUCED CHI SQUARE: 0.227 D OF F: 8

CODE SOURCE FLG UG/M3 %

1	TRANS	*	0.047+-	0.029	0.168+-	0.108
14	GEO-L	*	13.325+-	1.106	48.021+-	6.500
26	LIME	*	1.035+-	0.413	3.730+-	1.542
63	NDBLD	*	3.334+-	0.864	12.016+-	3.370
67	BLFUP	*	0.427+-	0.201	1.541+-	0.743
74	CUKST	*	7.929+-	0.962	28.576+-	4.622

TOTAL:			26.097+-	1.763	94.052+-	11.897
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SPECIE CODE	MEAS.	COARSE UG/M3	SUSPENDED PERCENT	PARTICULATE CALC. UG/M3	RATIO			
1 AL *	1.127+-	0.131	4.061	1.182+-	0.112	1.049+-	0.145	AL
2 SI *	3.853+-	0.443	13.887	3.889+-	0.376	1.009+-	0.139	SI
3 P	0.045+-	0.006	0.163	0.055+-	0.004	1.210+-	0.131	P
4 S	0.444+-	0.072	1.600	0.717+-	0.052	1.616+-	0.223	S
5 CL	0.015+-	0.005	0.054	0.199+-	0.017	9.999+-	9.999	CL
6 K *	0.317+-	0.038	1.143	0.296+-	0.026	0.932+-	0.114	K
7 CA *	0.895+-	0.103	3.226	0.893+-	0.056	0.998+-	0.088	CA
8 TI *	0.064+-	0.007	0.231	0.065+-	0.012	1.019+-	0.260	TI
9 V	0.005+-	0.001	0.019	0.004+-	0.000	0.655+-	0.090	V
10 CR	0.007+-	0.001	0.025	0.009+-	0.001	1.332+-	0.142	CR
11 MN *	0.026+-	0.003	0.094	0.029+-	0.002	1.104+-	0.133	MN
12 FE *	0.944+-	0.108	3.402	0.887+-	0.072	0.940+-	0.105	FE
13 NI *	0.023+-	0.003	0.084	0.021+-	0.002	0.910+-	0.097	NI
14 CU *	4.253+-	0.483	15.326	4.565+-	0.430	1.074+-	0.148	CU
15 ZN *	0.383+-	0.052	1.382	0.369+-	0.022	0.962+-	0.080	ZN
16 AS *	0.056+-	0.010	0.202	0.056+-	0.004	1.000+-	0.091	AS
17 SE	0.002+-	0.000	0.006	0.002+-	0.000	1.078+-	0.191	SE
18 BR *	0.009+-	0.001	0.032	0.009+-	0.001	1.001+-	0.203	BR
19 SR	0.012+-	0.001	0.043	0.010+-	0.001	0.863+-	0.075	SR
20 PD	0.002+-	0.001	0.006	0.004+-	0.001	2.485+-	1.536	PD
21 AG	0.013+-	0.002	0.047	0.009+-	0.001	0.655+-	0.121	AG
22 CD *	0.062+-	0.014	0.225	0.066+-	0.004	1.057+-	0.105	CD
23 IN	<	0.003	---	0.000+-	0.002	0.261+-	0.944	IN
24 SH	0.038+-	0.006	0.138	0.014+-	0.003	0.371+-	0.073	SH
25 SB	0.050+-	0.009	0.179	0.037+-	0.005	0.739+-	0.126	SB
26 BA	<	0.015	---	0.004+-	0.012	0.000+-	0.000	BA
27 HG	0.002+-	0.001	0.006	0.003+-	0.001	1.752+-	0.700	HG
28 PB *	0.860+-	0.111	3.098	0.841+-	0.053	0.979+-	0.086	PB

MEAS. AMB. MASS (UG/M3): 27.7

* - FITTING ELEMENT

Figure 30. Example CMB Printout

date (April 12, 1982) and the site code (4). The fourth line gives the sampling duration (48 hours) and the fifth line gives the sample site name (Hadfield). (The descriptive information which is provided for the quarterly means is, of course, slightly different but similar enough to the single sample format to be self-evident). After the descriptive information, the next line gives the reduced chi-square (0.227) and the number of degrees of freedom (8). The reduced chi-square is a statistical measure of the quality of the fit and the number of degrees of freedom is simply the difference between the number of fitting elements and the number of source fit ($14 - 6 = 8$, in this case). The closer the reduced chi-square is to zero, the better the CMB fit is considered. In practice a reduced chi-square value of less than one is considered excellent and less than five is considered usable. The greater the number of degrees of freedom for a given reduced chi-square value, the more statistically sound is the fit.

The information between the top two broken parallel lines is the source data. The numbers in the extreme left hand column are computer ID numbers for the sources which were fit. The second column lists the abbreviated source names. In this example these are: TRANS - transportation or vehicular exhaust, GEO-L - road dust composite L, LIME - limestone or lime rock, NDBLD - New Deal Building, i.e., fugitive ore concentrate and residue emissions, BLFUP - blast furnace upset and CUKST - American Chemet's copper kiln stack. The next two columns list the mass concentration assigned to each source and the percentage that is of the total filter mass concentration. For example, GEO-L contributed $13.325 \pm 1.106 \mu\text{g}/\text{m}^3$ to the ambient aerosol which was 48.021 ± 6.500 percent of the total. Immediately below the second broken line the total mass concentration assigned to the sources ($26.097 \pm 1.763 \mu\text{g}/\text{m}^3$) and the percentage that is of the total filter mass ($94.052 \pm 11.897\%$) are listed.

The information contained between the second set of broken parallel lines is the elemental data. The column on the extreme left is the computer element code. Twenty-eight elements were used in the CMB fits presented here. The second column from the left lists their chemical symbols. If an

asterisk appears in the third column, then the element was used as a fitting element. Elements with a measured concentration considerably higher than the uncertainty associated with the measurement are, as a general rule, used as fitting elements. Also elements which are key indicating elements are included as fitting elements even when their concentrations are relatively low (e.g., Br for automobile exhaust). Phosphorous and chlorine were not used as fitting elements in this study. It is difficult to obtain a good standard for phosphorous, hence there is some uncertainty as to its absolute accuracy. Chlorine was not used as it seemed to vary independently from the other sources, i.e., it did not fit well and it was generally at a moderately low concentration. A number of metallurgical fluxes contain chlorine (chloride) at high concentrations and this may be the source of the variable chlorine content seen in the ambient samples. Sulfur was not used as a fitting element in the coarse and total size fraction due to the identification by XRD of sulfate artifact compounds as previously mentioned. Data for elements which are not selected as fitting elements are calculated and listed on the printout but these non-selected elements put no statistical fitting pressure on the multielement least square fitting program.

The column immediately to the right of the chemical symbols and asterisk (if present) lists the measured concentration and associated uncertainty of each element in $\mu\text{g}/\text{m}^3$. For example, $0.944 \pm 0.108 \mu\text{g}/\text{m}^3$ was the concentration of iron determined from analyses of the ambient filter and the volume of air sampled by that filter. The next column lists the calculated concentration of each element which was determined by the CMB modelling. The calculated concentration for iron in this case was $0.887 \pm 0.072 \mu\text{g}/\text{m}^3$. The next to the last column gives the ratio (and the associated uncertainty) of the calculated concentration to the measured concentration. For iron, in this case, the ratio is 0.940 ± 0.105 , i.e., $(0.887 \pm 0.072 \mu\text{g}/\text{m}^3) / (0.944 \pm 0.108 \mu\text{g}/\text{m}^3)$. The closer the ratio of calculated to measured mass is to unity for each element the better is the CMB fit. In practice ratios of .8 to 1.2 are considered to be very good, however it must be emphasized when reviewing the ratios that elements with low concentrations, high uncertainties or with less than concentration values (e.g., Pd, In and Ba in this case)

will regularly produce ratios outside those limits. The last column simply relists the chemical symbols for the elements again for convenience. Finally, below the bottom broken line the total mass concentration is given which is determined from the mass on the filter and volume of air sampled. The value for this filter is $27.7 \mu\text{g}/\text{m}^3$. The uncertainty associated with the mass concentration is dominated by the uncertainty in the air volume measurement which generally is around $\pm 10\%$.

The quality of CMB fits are judged by the combination of three factors: (1) the reduced chi-square, (2) the ratio of calculated to measured mass for each element and (3) the percent of the total mass explained by the CMB calculations. By all three criteria the quarterly mean CMB fits given in Appendix I provide state-of-the-art source apportionment results. In nearly every case the reduced chi-square was less than five and in most cases it was less than one. In the few cases that the reduced chi-square was greater than five, (which occurred in fine fraction fits three times only) either the addition of the residential wood combustion source would drop the reduced chi-square value (with a concomitant overprediction of mass) or apparently not all the appropriate source fingerprints were in the source matrix (the fine fraction at the Microwave site, second quarter). Additionally, approximately 50% or more of the fine fraction mass and 70% or more of the coarse and total fraction mass were regularly explained by the CMB fits. These levels of assigned mass are typical of values obtained in other airsheds and it should be recalled that a high organic and elemental carbon content in East Helena ambient aerosols has been measured (Table 32). Finally, the calculated to measured ratios for the principal geological and mineralogical elements were in most cases close to unity which demonstrates that the contribution of the key industrial and fugitive dust sources has been well defined.

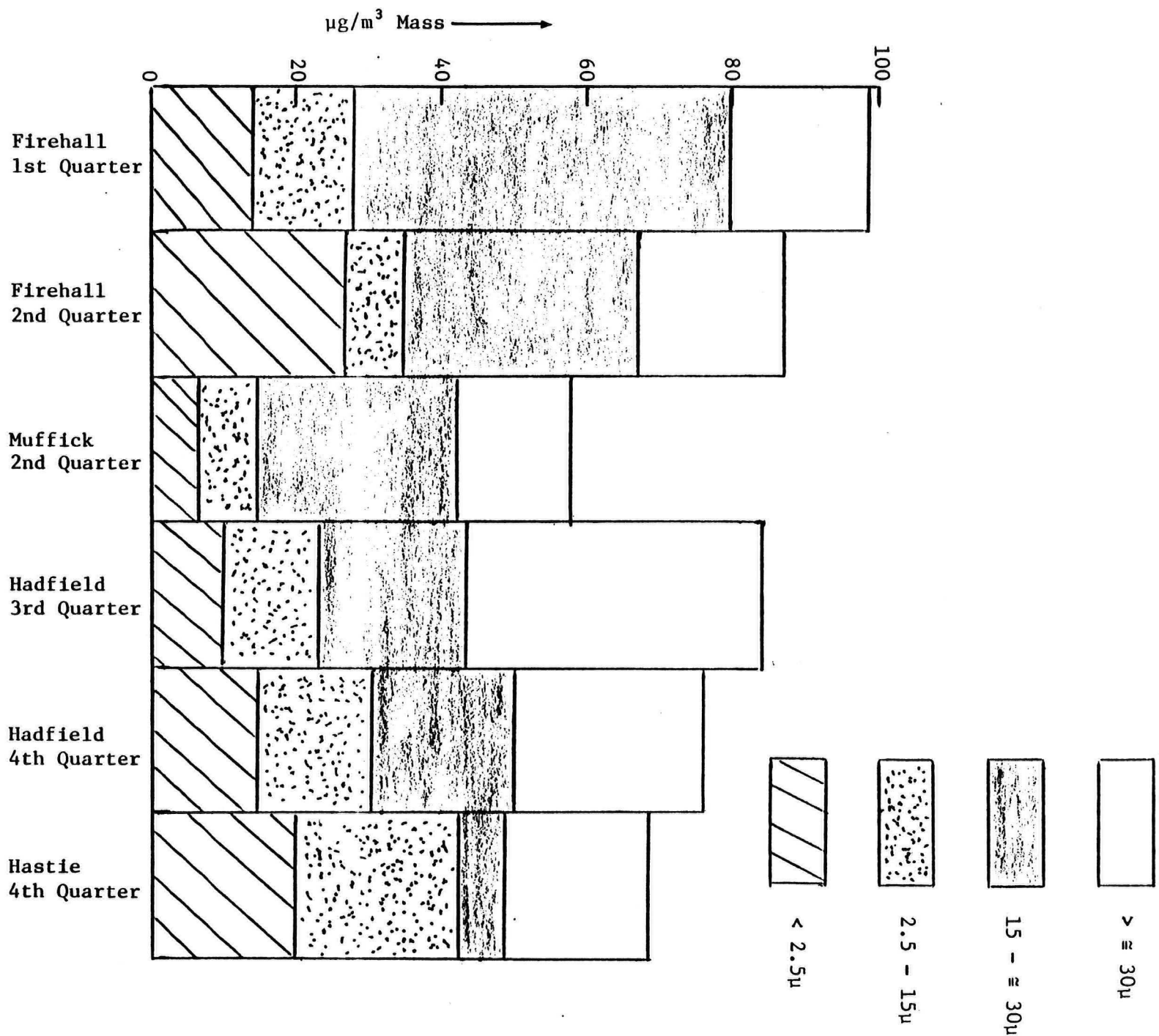
3.4 Supplemental Data

Several types of supplemental data are available to support and further understand the CMB source apportionment results. These are: (1) elemental and mass size distributions, (2) bivariate plots, (3) meteorological observations and (4) information from other studies.

The lead and mass size distribution in ambient aerosols collected at the key ambient monitoring sites are presented in Figures 31 and 32. Quarterly mean values were used to construct the figures. The Highway site was not included in Figures 31 and 32 since no hi-vol sampler was operated there. The less than 2.5μ size is from measurements made on the coarse and lead measurements made on the fine fraction dichotomous sampler filters. The 2.5μ to 15μ size is from measurements made on the coarse fraction dichotomous sampler filters. The 15μ to $\approx 30\mu$ size fraction is the difference in values measured on lo-vol sampler filters and those obtained from the sum of the two dichotomous filters. The greater than $\approx 30\mu$ size fraction is the difference in values measured on hi-vol sampler filters and lo-vol sampler filters. As can be seen in Figures 31 and 32, a large portion of the mass and lead content in the East Helena ambient aerosols is in particles greater than 15μ and a smaller but significant fraction is in particles greater than $\approx 30\mu$. This implies that fugitive emissions are at least one important source of ambient lead and mass concentrations which is consistent with the CMB source apportionment results presented in Figures 23 through 29.

In addition to mass and lead hi-vol values, data for cadmium, copper, zinc and arsenic were also available from hi-vol samples collected in the fourth quarter of 1981. Table 34 lists the mean ratios of mass, Pb, Cd, Cu, Zn and As measured on lo-vol samples to that measured on co-collected hi-vol samples. As previously discussed, a significant fraction of lead and mass was found in the size fraction $>\approx 30\mu$ which is reflected in the ratios for mass and lead given in Table 34.

Figure 31 SIZE DISTRIBUTION OF AMBIENT TSP CONTENT BY QUARTER



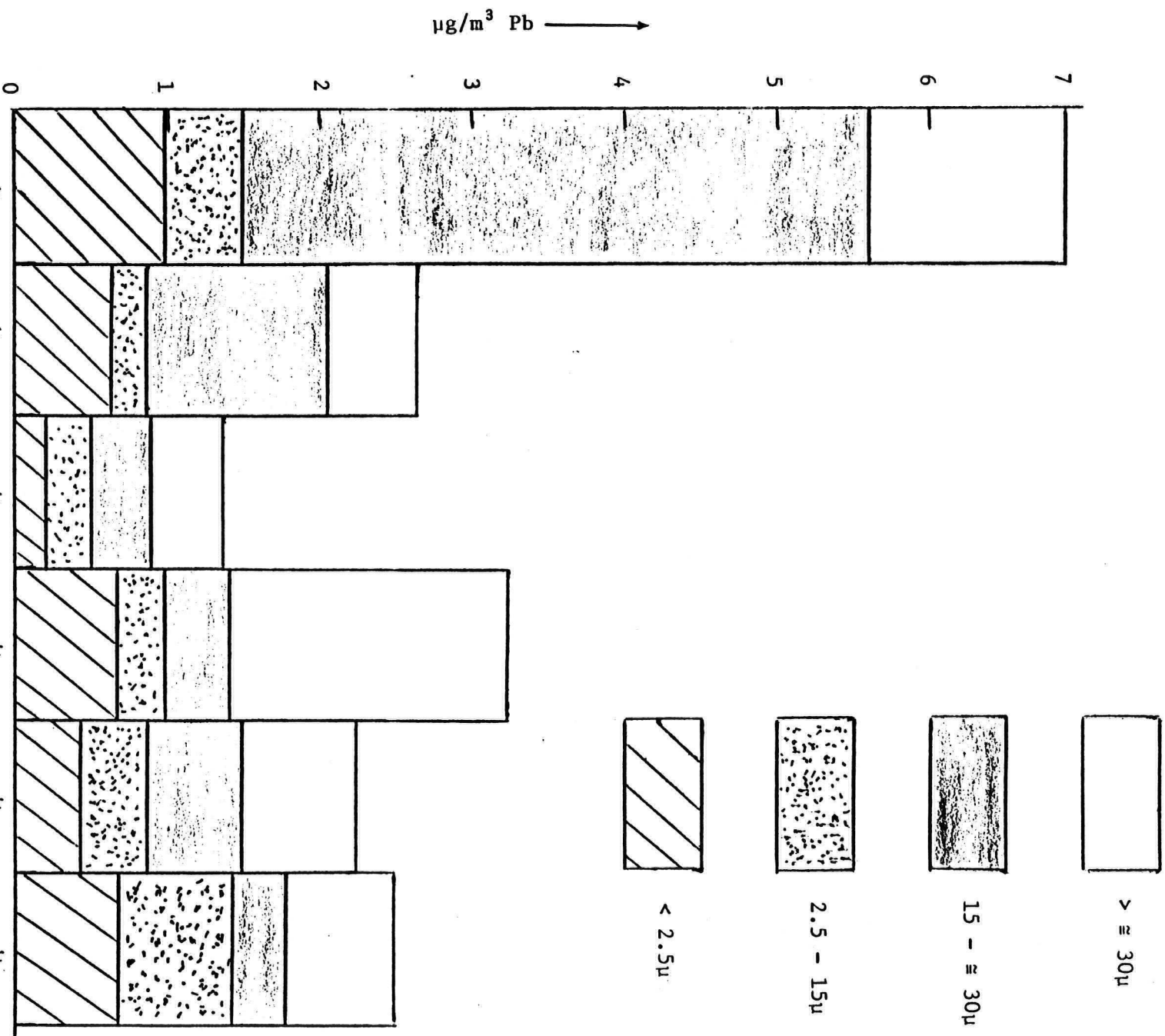


Figure 32

SIZE DISTRIBUTION OF AMBIENT Pb CONTENT BY QUARTER

Table 34

LO-VOL / HI-VOL RATIO OF MASS, Pb, Cd, Cu, Zn & As CONCENTRATIONS FROM CO-COLLECTED SAMPLES

Sample Set	Mass	Pb	Cd	Cu	Zn	As
Hadfield 4th Quarter 28 Sample Days	.66	.69	1.05	.66	1.06	1.33
Hastie 4th Quarter 23 Sample Days	.65	.71	1.05	.56	.96	1.32

A large fraction of the copper content is also in the $\geq 30\mu$ size category as can be seen by the ratios in Table 34. American Chemet's copper kiln and contaminated road and soil dusts have been shown by the CMB modelling to be major sources of copper in the East Helena airshed. The fact that a significant fraction of ambient copper-containing particles are $\geq 30\mu$ is consistent with three observations made by the author: (1) the TSP copper kiln source sample was "grainy" in appearance, i.e., some very large particles were collected, (2) the short copper kiln stack can and literally does on occasion fumigate East Helena at near ground level (i.e., not a dispersion effect but a direct impact), and (3) fugitive emissions were noted being emitted through openings and windows in the copper processing portion of the American Chemet plant.

The lo-vol to hi-vol ratios for arsenic are informative even though there is clearly a small analytical determinate error between the arsenic values measured on hi-vol glass fiber filters and those determined from the lo-vol teflon filters since the calculated ratios in Table 34 are greater than one. Arsenic traditionally has been problematic to determine by atomic spectrophotometric means due to the loss of volatile arsenic compounds during digestion and storage of samples prior to analyses. It is possible that the arsenic values determined from the hi-vol filters are slightly lower than the values determined from the lo-vol filters by XRF due to that volatility problem. It is, however, worth noting that the hi-vol and lo-vol arsenic values are well within the standard deviations of each other (Table 30) at all four sites (Hadfield, Hastie, Padbury and South) where co-collected lo-vol and hi-vol arsenic data were available. The closeness of the values determined by two independent laboratories with two different sample types and by two totally different techniques would, under most circumstances, be considered a mark of excellent agreement. It is also worth noting that at those locations where a dichotomous sample set was collected along with a hi-vol and lo-vol set that more than half the arsenic was in the less than 2.5μ size category. This is reasonable in light of the fact that the dross building emissions

were identified by CMB source apportionment to be a source of lead and TSP and that the fine fraction source fingerprint for the dross building contained a very high arsenic content (58% by weight). Comparison of the relative mass contained in the three size fractions of source samples multiplied by their arsenic content also revealed that well over half the arsenic's absolute mass emitted from the dross building was associated with particles less than 2.5μ in aerodynamic diameter. Arsenic originating from other sources would similarly tend to be enriched in the finer particles due to the volatile/condensable nature of arsenic.

Perhaps the most useful information contained in Table 34 are the ratios for cadmium and zinc. An insignificant amount of cadmium and zinc occur in particles greater than $\approx 30\mu$ at the two key sites since the ratios in Table 34 are near unity. This implies windblown dust or particles mechanically resuspended are probably not the most important sources of cadmium or zinc. The blast furnace upset has been identified as being a major source of lead by CMB source apportionment and one of two sources containing a high cadmium concentration (the other source of high cadmium is the baghouse stack). Review of Tables 19 through 29 reveal that in all cases where there are co-collected dichotomous/hi-vol sets (Hadfield, Hastie and South sites, fourth quarter) more than one half of the cadmium as with arsenic is in particles with aerodynamic diameters of less than 2.5μ . Comparison of the relative mass of each of the three size fractions of source samples of blast furnace upset emissions multiplied by their respective cadmium content shows that the majority of the mass of cadmium from blast furnace upsets is in the $<2.5\mu$ size fraction. In addition, while it is difficult to directly compare data characterizing blast furnace upset samples collected more than four years apart due to the non-uniform nature of upsets, a single sample of blast furnace upset emissions collected in 1977 by researchers from the Midwest Research Institute⁶ also revealed that well over half the cadmium mass is in particles with diameters of less than 2.5μ (aerodynamic, i.e., normalized to $\rho = 1/\text{cm}^3$). As with mass, lead and arsenic the size distribution observed for cadmium is consistent with the CMB source apportionment results.

The fact that few zinc rich particles of greater than $\approx 30\mu$ occur in the aerosols collected at the Hadfield and Hastie sites during the fourth quarter suggests that the zinc oxide material identified to contribute to ambient mass and lead concentrations is predominately from process fugitive emissions rather than windblown or mechanically resuspended zinc oxide fume product handled and stored by both ASARCO and American Chemet. Two process fugitive emission sources of zinc oxide material have been identified. These are ASARCO's zinc fuming furnace building (zinc plant) and the American Chemet's zinc kiln discharge vent. The emissions from ASARCO's zinc plant are dramatically greater than from the American Chemet's zinc kiln discharge vent. This coupled with the observation that the level of impact of the zinc oxide material was nearly ten times as great at the Hastie site as it was at the Hadfield site during the fourth quarter and the Hastie site is nearest ASARCO's zinc plant whereas the Hadfield site is nearest to American Chemet's zinc kiln discharge further indicates that the predominate source of zinc oxide material is from ASARCO's zinc plant.

While an extensive correlation between meteorological conditions and ambient aerosol levels requires sophisticated statistical analysis due to the number of variables in a situation such as is encountered in East Helena and is beyond the scope of this report, a single and simple example of the effect of wind direction is presented here. Figures 33 and 34 are CMB fits of 24 hour 10-vol TSP samples collected at the Muffick site on June 15 and June 18, 1981, respectively. The average wind speed on June 15 was 9.8 mph, the resultant wind speed was 8.1 mph and the resultant direction was from the west (as measured at the Helena airport). The average wind speed on June 18 was 6.0 mph, the resultant wind speed was 0.2 mph and the resultant direction was from the northwest. Average wind speed is a scalar average, resultant wind speed is a vector average. A low resultant wind speed implies that winds were not consistently from a given direction during the 24 hour averaging period and their vectors cancel each other. The National Weather Service measurements at 2:00 p.m.

CMBDEQ RESULTS FOR CMB # HT129

TOTAL PARTICULATE FRACTION

SAMPLING DATE: 810615 SITE CODE: 09

SAMPLING DURATION: 24 HRS. WITH START HOUR: 0

SITE: MUFFICK

EFFECTIVE VARIANCE FITTING. REDUCED CHI SQUARE: 0.579 D OF F: 8

CODE SOURCE FLG UG/M3 %

1	TRANS	*	0.272+-	0.119	0.606+-	0.273
14	GEO-L	*	22.758+-	1.505	50.762+-	6.169
26	LIME	*	2.275+-	0.647	5.074+-	1.533
65	DRBLD	*	0.435+-	0.103	0.971+-	0.250
73	ZHKLD	*	0.223+-	0.087	0.498+-	0.200
74	CUKST	*	2.057+-	0.419	4.588+-	1.045

TOTAL:			28.021+-	1.700	62.499+-	7.416
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SPECIE CODE	MEAS. UG/M3	SUSPENDED PARTICULATE PERCENT	CALC. UG/M3	RATIO
1 AL *	1.643+- 0.197	3.665	1.880+- 0.185	1.144+-0.171 AL
2 SI *	5.899+- 0.668	13.157	6.663+- 0.659	1.129+-0.168 SI
3 P	0.079+- 0.013	0.177	0.051+- 0.005	0.637+-0.070 P
4 S	0.775+- 0.115	1.730	0.322+- 0.022	0.415+-0.031 S
5 CL	0.043+- 0.019	0.096	0.067+- 0.005	1.573+-0.223 CL
6 K *	0.400+- 0.051	0.891	0.387+- 0.038	0.968+-0.132 K
7 CA *	1.327+- 0.153	2.961	1.328+- 0.092	1.000+-0.098 CA
8 TI *	0.104+- 0.014	0.233	0.091+- 0.009	0.874+-0.114 TI
9 V	0.007+- 0.003	0.015	0.006+- 0.001	0.887+-0.116 V
10 CR	0.004+- 0.003	0.009	0.006+- 0.001	1.482+-0.245 CR
11 MN *	0.030+- 0.005	0.068	0.029+- 0.003	0.956+-0.128 MN
12 FE *	1.191+- 0.136	2.656	1.070+- 0.105	0.899+-0.119 FE
13 NI *	0.013+- 0.003	0.030	0.010+- 0.001	0.763+-0.063 NI
14 CU *	1.693+- 0.191	3.775	1.760+- 0.128	1.040+-0.109 CU
15 ZN *	0.385+- 0.045	0.858	0.386+- 0.027	1.004+-0.101 ZN
16 AS *	0.137+- 0.021	0.306	0.139+- 0.013	1.015+-0.140 AS
17 SE	0.004+- 0.002	0.008	0.002+- 0.000	0.616+-0.079 SE
18 BR *	0.023+- 0.004	0.052	0.024+- 0.007	1.010+-0.429 BR
19 SR	0.013+- 0.003	0.030	0.010+- 0.001	0.743+-0.086 SR
20 PD	< 0.006	---	0.006+- 0.001	3.059+-1.670 PD
21 AG	< 0.011	---	0.007+- 0.001	0.845+-0.216 AG
22 CD *	0.039+- 0.020	0.088	0.020+- 0.002	0.513+-0.061 CD
23 IN	< 0.017	---	0.001+- 0.002	0.075+-0.127 IN
24 SH	0.037+- 0.020	0.082	0.014+- 0.002	0.370+-0.069 SH
25 SB	< 0.040	---	0.030+- 0.005	2.346+-1.006 SB
26 BA	< 0.086	---	0.012+- 0.010	0.382+-0.340 BA
27 HG	< 0.003	---	0.003+- 0.000	1.847+-0.699 HG
28 PB *	0.505+- 0.059	1.126	0.507+- 0.039	1.004+-0.108 PB

MEAS. AMB. MASS (UG/M3): 44.8

* - FITTING ELEMENT

Figure 33 CMB Printout, Muffick Site, June 15, 1981

CMBDEQ RESULTS FOR CMB # HT131

TOTAL PARTICULATE FRACTION

SAMPLING DATE: 810618 SITE CODE: 09

SAMPLING DURATION: 24 HRS. WITH START HOUR: 0

SITE: MUFFICK

EFFECTIVE VARIANCE FITTING. REDUCED CHI SQUARE: 1.257 D OF F: 7

CODE SOURCE FLG UG/M3 %

1	TRANS	*	0.947+-	0.402	1.818+-	0.794
14	GED-L	*	25.558+-	1.816	49.071+-	6.099
26	LIME	*	2.002+-	0.681	3.845+-	1.366
65	DRBLD	*	2.279+-	0.479	4.375+-	1.022
67	BLFUP	*	4.041+-	0.605	7.753+-	1.405
73	ZHKLD	*	1.471+-	0.321	2.824+-	0.681
74	CUKST	*	5.120+-	0.854	9.831+-	1.921

TOTAL:			41.418+-	2.313	79.522+-	9.246
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SPECIE CODE	MEAS. UG/M3	SUSPENDED PARTICULATE PERCENT	CALC. UG/M3	RATIO
1 AL *	1.902+- 0.228	3.651	2.125+- 0.207	1.117+-0.164 AL
2 SI *	6.454+- 0.730	12.392	7.495+- 0.740	1.161+-0.176 SI
3 P	0.129+- 0.019	0.248	0.093+- 0.006	0.720+-0.057 P
4 S	1.561+- 0.234	2.998	1.098+- 0.085	0.703+-0.066 S
5 CL	0.153+- 0.039	0.294	0.307+- 0.042	2.003+-0.616 CL
6 K *	0.535+- 0.069	1.027	0.510+- 0.043	0.954+-0.111 K
7 CA *	1.400+- 0.161	2.688	1.403+- 0.094	1.003+-0.095 CA
8 TI *	0.105+- 0.015	0.202	0.106+- 0.010	1.004+-0.135 TI
9 V	0.007+- 0.003	0.014	0.007+- 0.001	0.918+-0.121 V
10 CR	0.009+- 0.003	0.018	0.008+- 0.001	0.911+-0.092 CR
11 MN *	0.051+- 0.007	0.099	0.034+- 0.003	0.665+-0.074 MN
12 FE *	1.397+- 0.159	2.682	1.287+- 0.119	0.921+-0.115 FE
13 NI *	0.023+- 0.004	0.044	0.023+- 0.001	1.025+-0.079 NI
14 CU *	3.606+- 0.405	6.924	3.580+- 0.286	0.993+-0.112 CU
15 ZN *	1.504+- 0.170	2.887	1.484+- 0.100	0.987+-0.093 ZN
16 AS *	0.727+- 0.087	1.397	0.716+- 0.069	0.984+-0.134 AS
17 SE	0.010+- 0.003	0.019	0.012+- 0.001	1.210+-0.125 SE
18 BR *	0.078+- 0.010	0.150	0.075+- 0.025	0.965+-0.440 BR
19 SR	0.021+- 0.004	0.041	0.014+- 0.001	0.652+-0.062 SR
20 PD	< 0.007	---	0.033+- 0.003	8.723+-6.415 PD
21 AG	0.021+- 0.012	0.040	0.022+- 0.002	1.068+-0.140 AG
22 CD *	0.544+- 0.073	1.045	0.460+- 0.041	0.845+-0.100 CD
23 IN	< 0.017	---	0.007+- 0.002	0.718+-0.275 IN
24 SN	0.093+- 0.025	0.179	0.058+- 0.004	0.619+-0.054 SN
25 SB	0.069+- 0.047	0.132	0.103+- 0.011	1.503+-0.285 SB
26 BA	0.299+- 0.106	0.574	0.025+- 0.012	0.082+-0.040 BA
27 HG	0.008+- 0.005	0.015	0.007+- 0.001	0.901+-0.163 HG
28 PB *	2.438+- 0.275	4.680	2.791+- 0.183	1.145+-0.114 PB

MEAS. AMB. MASS (UG/M3): 52.1

* - FITTING ELEMENT

Figure 34 CMB Printout, Muffick Site, June 18, 1981

and 5:00 p.m. on June 18 revealed that winds of 5 and 8 knots, respectively, were blowing from 120° (from the southeast). The Muffick site is north-northwest of the ASARCO and American Chemet plants. The increase in mineralogical elements and the concomitant increase in the mass designed to industrial sources on June 18 versus June 15 is apparent.

While the prevailing wind at East Helena is from the west, a wind rose reflecting long term averages (Figure 35) is nearly symmetrical around the east-west axis and it can be seen that during a significant minority of the time winds will be blowing from a southerly direction and the East Helena airshed will be subject to high industrial impact. A study conducted by the North American Weather Consultants also revealed southerly winds will often occur during winter months in the morning hours.¹³ A downwash effect across the slag pile was also noted under these conditions.

Bivariant plots of elemental concentrations are useful in determining the sources of elements observed in ambient aerosols. Elements from which atmospheric concentrations are derived from a single major common source or from several major sources which contain them at similar concentrations will exhibit a very high linear correlation when their percent composition in ambient aerosols are plotted versus each other. Figures 36 and 37 are plots of percent aluminum versus percent silicon in 10-vol TSP samples collected at the Hadfield and Highway sites, respectively. Since the principal source of particles containing aluminum and silicon is road and soil dust, a very high correlation coefficient is obtained for their linear plots ($r^2 = .991$ for both plots) and the slope is an indicator of their relative abundance in the source ($Al/Si \approx .27$). When two elements have many common sources but no one source is predominate then some degree of correlation is obtained in linear bivariant plots. Figures 38 and 39 illustrate such cases. Most sources of lead contain arsenic and zinc but at different concentration levels and hence a strong correlation such as

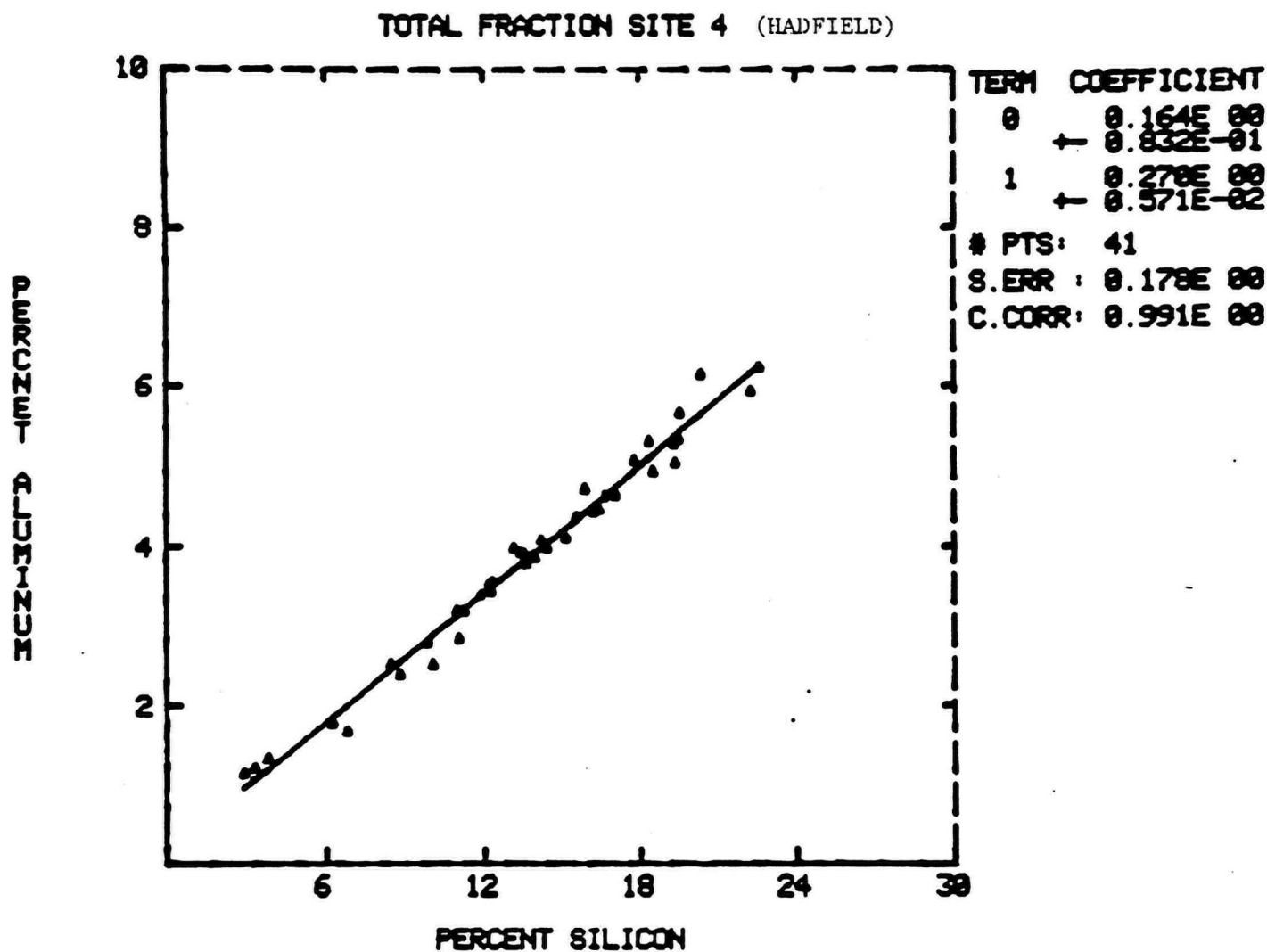


Figure 36 Bivariant Plot, Percent Al versus Percent Si
in Lo-Vol TSP Samples Collected at the Hadfield
Site

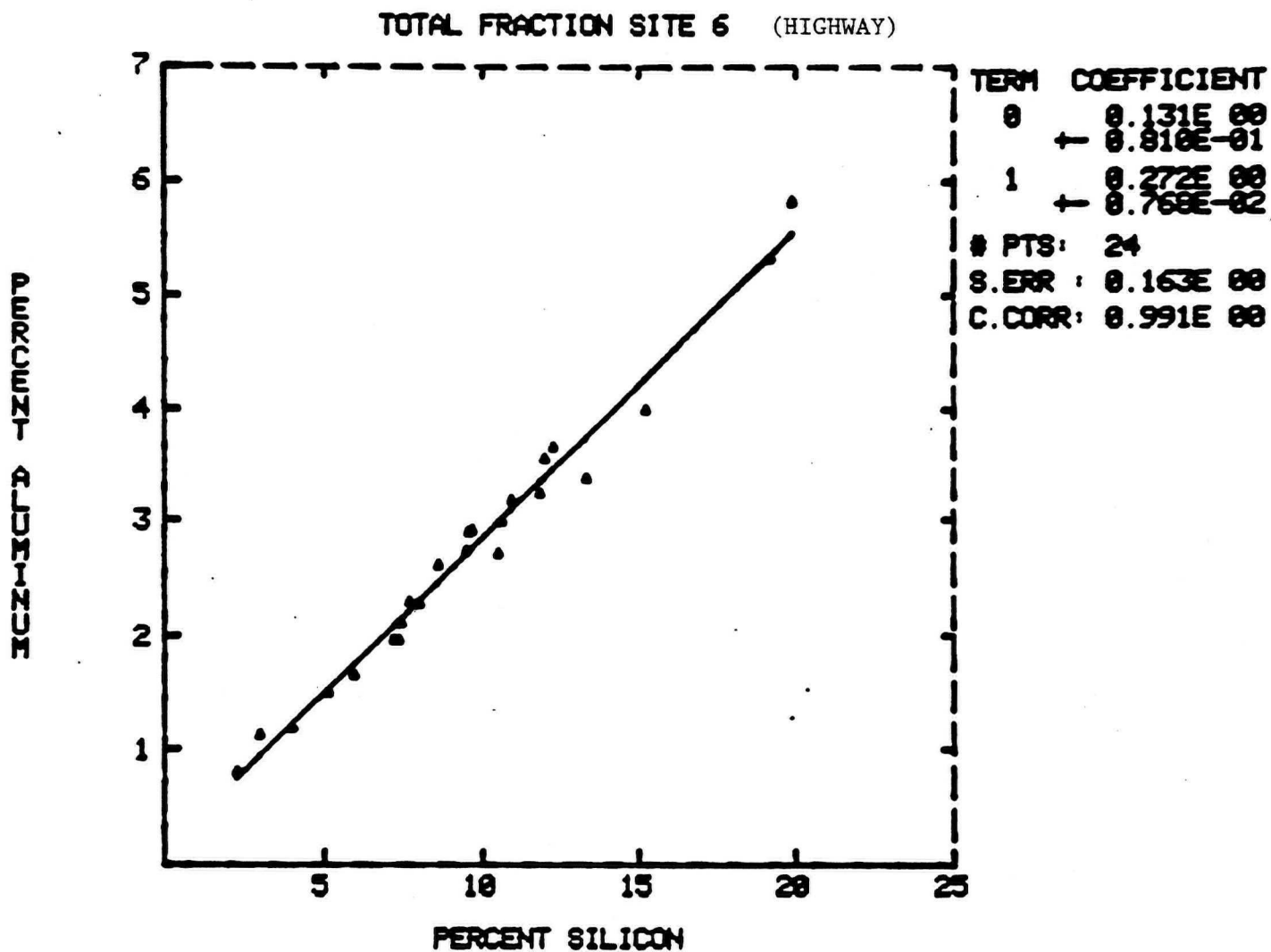


Figure 37 Bivariant Plot, Percent Al versus Percent Si
in Lo-Vol TSP Samples Collected at the Highway
Site

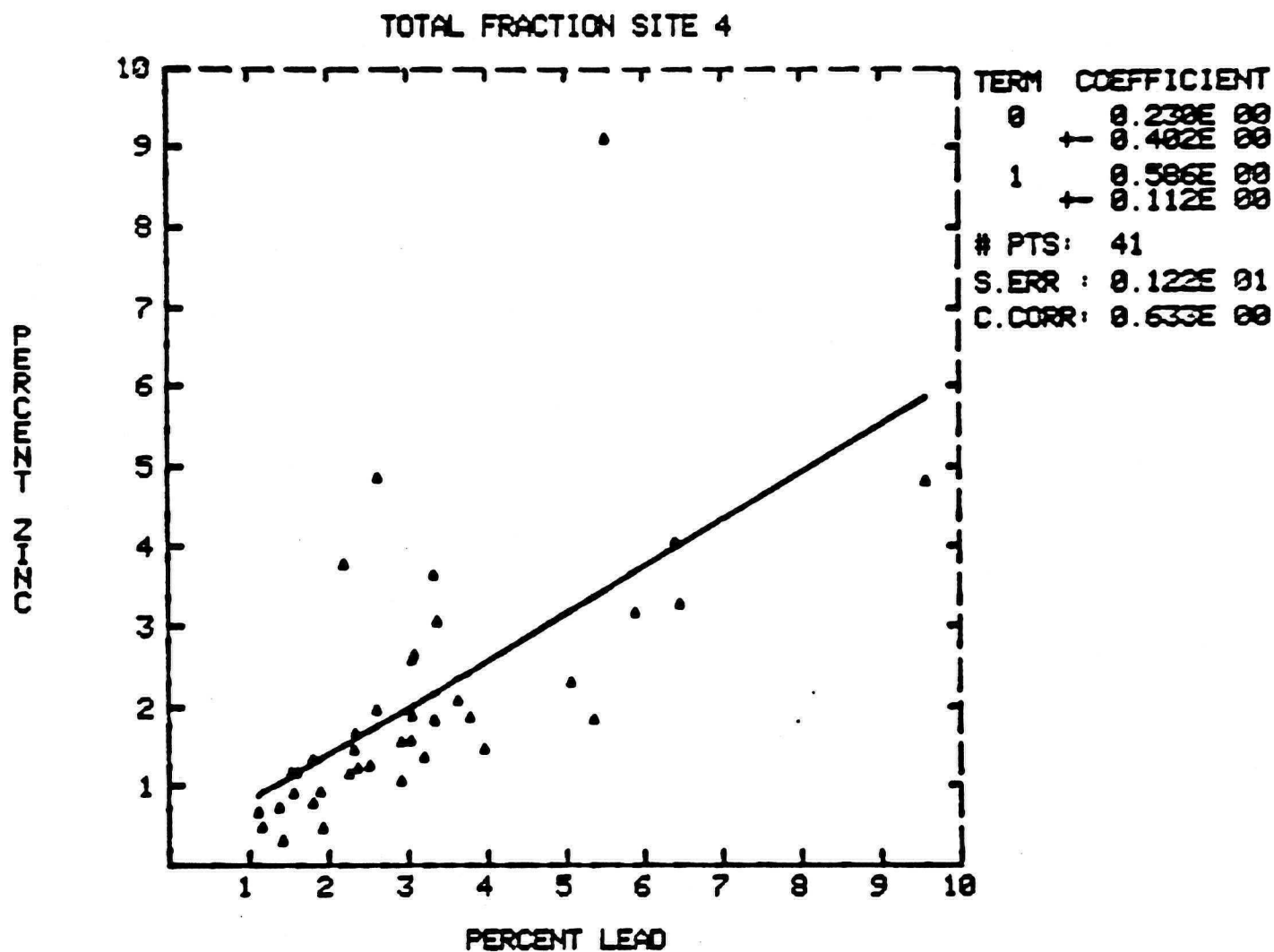


Figure 38 Bivariant Plot, Percent Zn versus Percent Pb
in Lo-Vol TSP Samples Collected at the Hadfield
Site

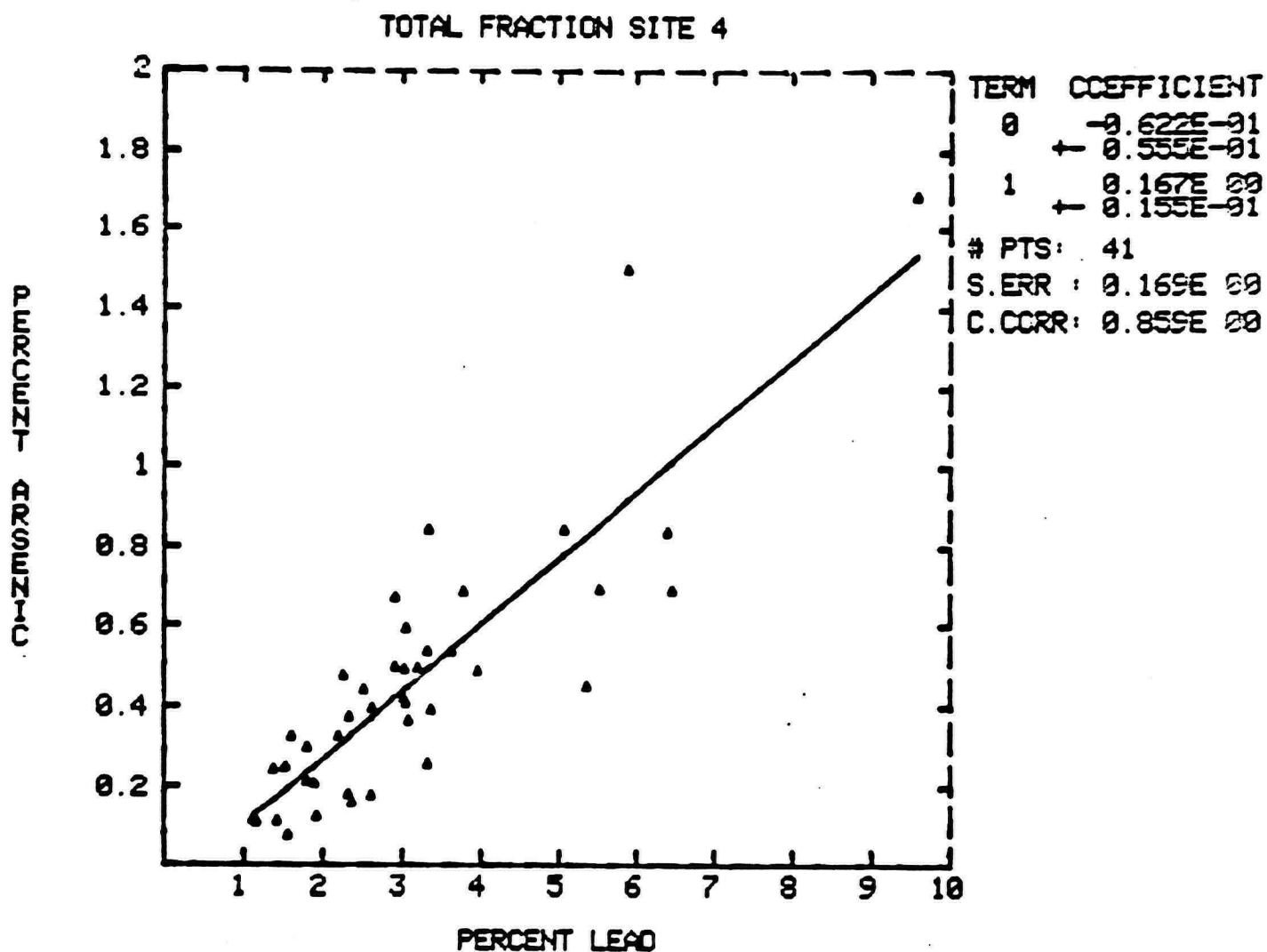


Figure 39 Bivariant Plot, Percent As versus Percent Pb
in Lo-Vol TSP Samples Collected at the Hadfield
Site

is seen with Al versus Si is not obtained for Zn versus Pb or As versus Pb. When two elements have few or no common sources, then a very poor correlation is seen. Plots of percent silicon versus percent lead show very poor correlations (Figures 40 and 41) since with the exception of contaminated road and soil dust, none of the lead sources contain high silicon concentrations. These latter two plots are particularly significant as there had been speculation at one time that the major source of lead may be resuspended road and soil dust. Figures 40 and 41 demonstrate that resuspended road and soil dust is not the single predominate source of lead in the East Helena airshed.

By reviewing long term data, the study year 1981 appears to be more or less typical in terms of ambient Pb and TSP levels and in terms of ASARCO's industrial activity (Table 35). Similarly, the fourth quarter of 1981 during which most of the ambient data was collected does not appear particularly unusual in comparison to the other quarters of 1981. (Figures 10 and 42). The Hastie site data was compiled in Table 35 since it is the only site at which sampling has been continuously conducted over a reasonable length of time necessary to detect any trends and it is a key site in the lead non-attainment area. A currently unexplained drop in ambient lead concentration occurred between 1978 and 1979 which merits further investigation. The ambient annual lead concentration during 1979, 1980 and 1981 has been remarkably constant and above $1.5 \mu\text{g}/\text{m}^3$. The annual geometric mean TSP has vacillated only modestly around the $75 \mu\text{g}/\text{m}^3$ standard during the seven year period tabulated in Table 35.

Based on the limited data available, the ambient aerosol in the East Helena non-attainment area during the study period appears to be representative of typical conditions and the results of this study should be generally applicable and carry no special caveat as to their usefulness.

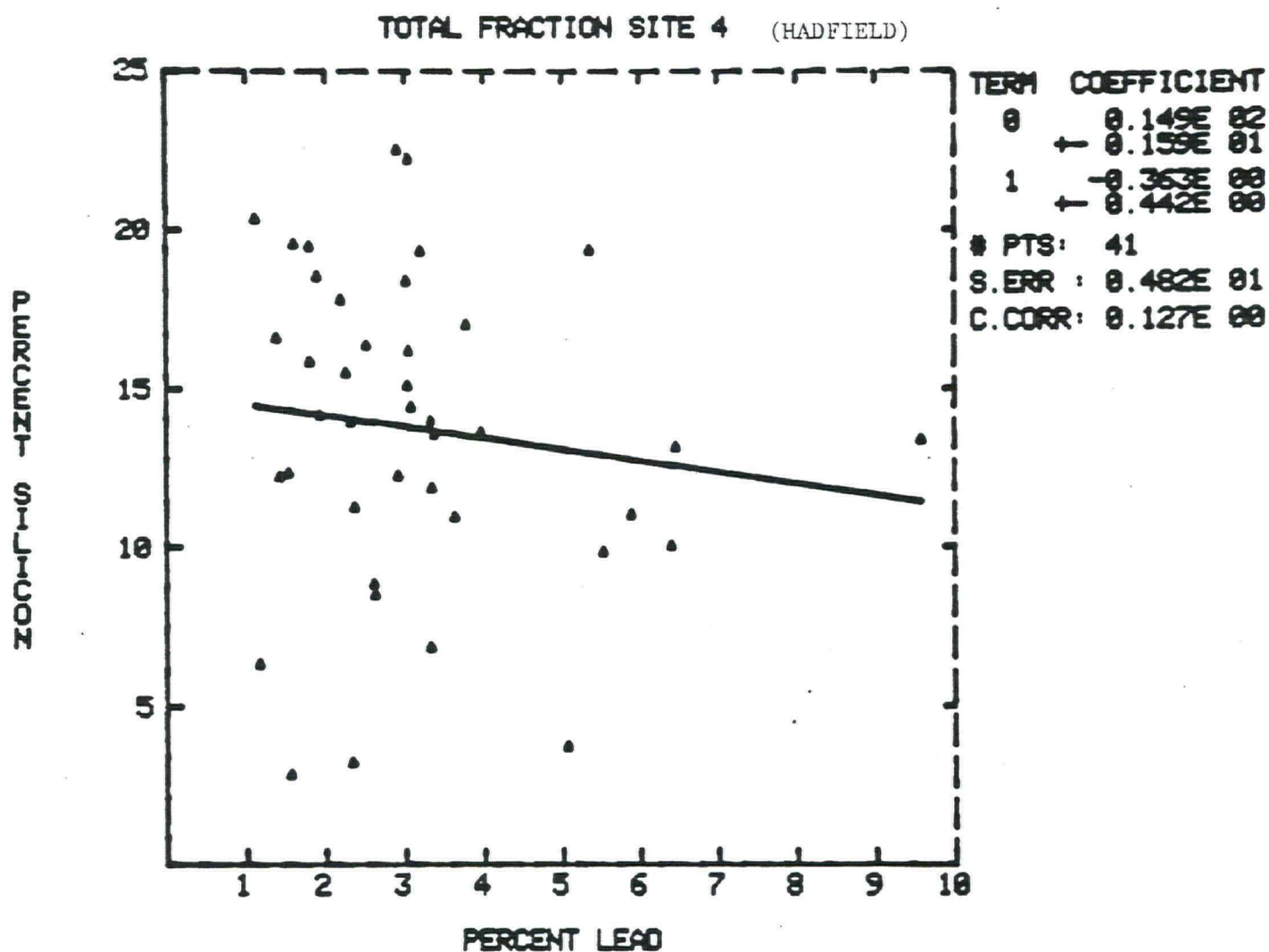


Figure 40 Bivariant Plot, Percent Si versus Percent Pb
 in Lo-Vol TSP Samples Collected at the Hadfield
 Site

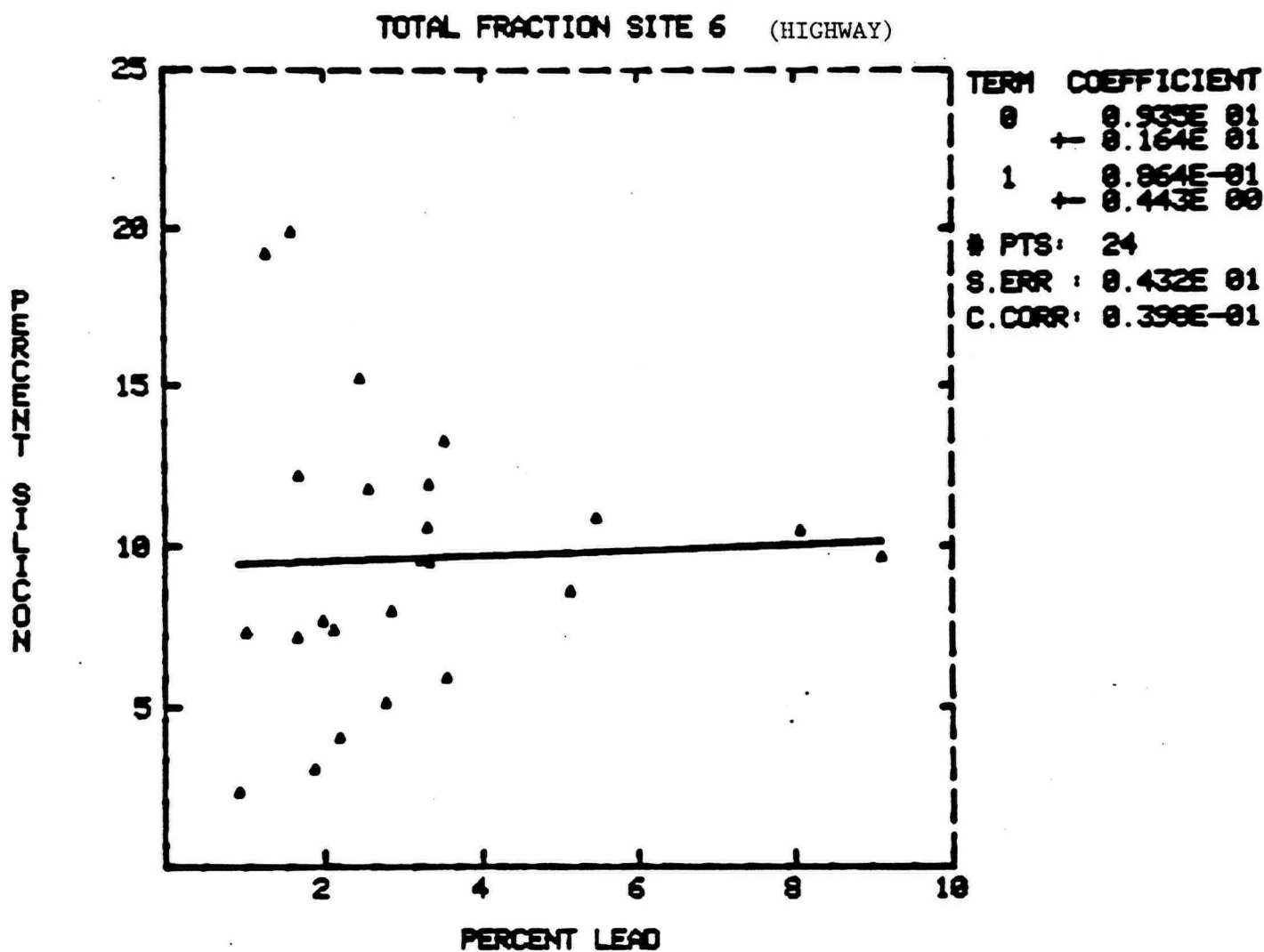


Figure 41 Bivariant Plot, Percent Si versus Percent Pb
in Lo-Vol TSP Samples Collected at the Highway
Site

Table 35

Annual Mean Lead and TSP Values Hastie Site
and Lead Production East Helena ASARCO Plant

Year	Mean TSP ($\mu\text{g}/\text{m}^3$)		Mean Pb ($\mu\text{g}/\text{m}^3$) Arithmetic	Lead Production (Tons)
	Geometric	Arithmetic		
1981	67	77	2.34	56,746
1980	86	93	2.41	52,988
1979	80	87	2.95	59,596
1978	77	88	4.30	56,463
1977	67	76	5.29	54,404
1976	74	83	--	64,280
1975	64	77	--	58,558

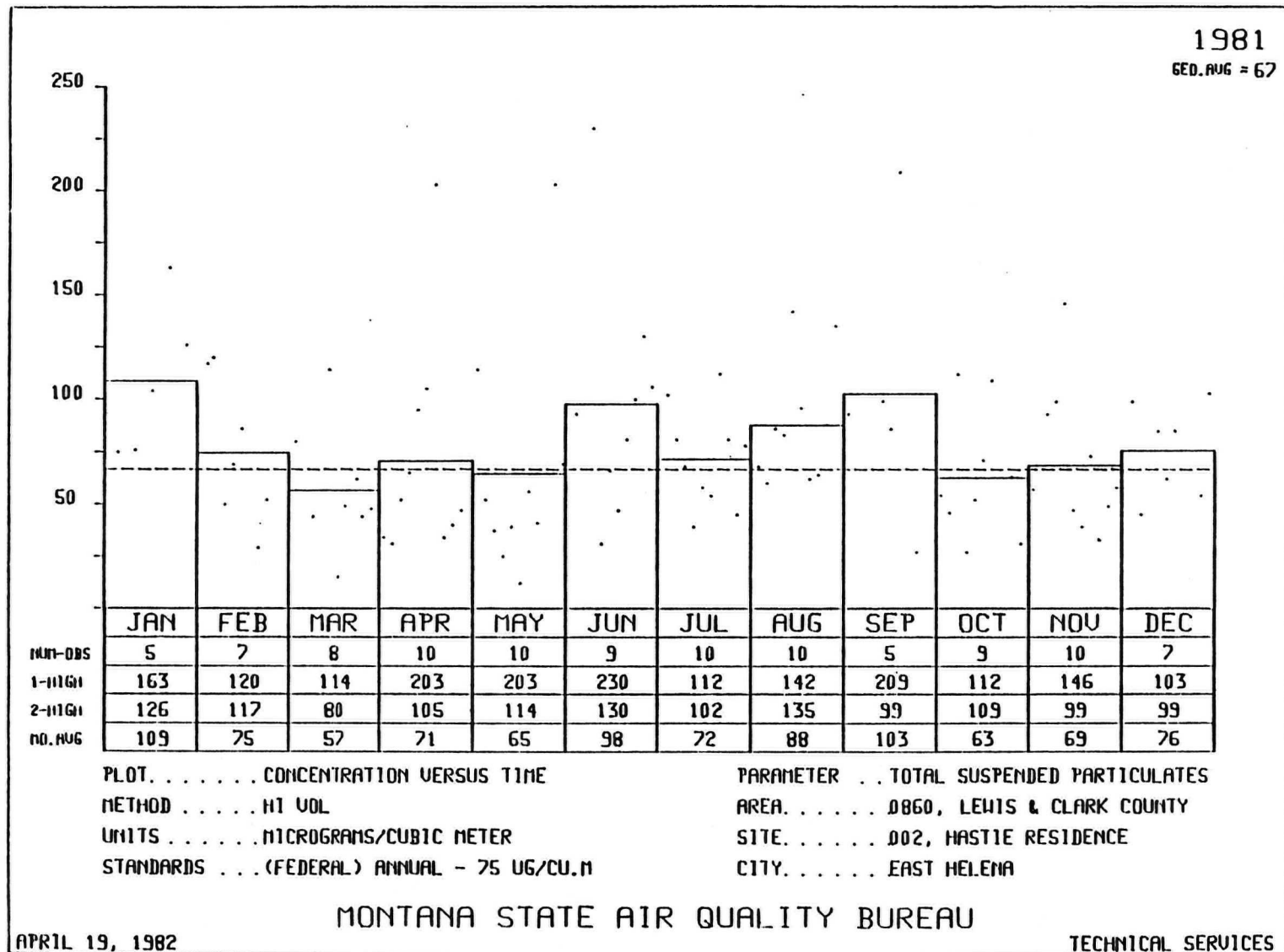


Figure 42 Ambient TSP Concentrations Measured on Hi-Vol Samples - Hastie Site

4.0 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

By reviewing the ambient data, the source data, the results of the CMB source apportionment and the supplemental data the following conclusions have been reached:

1. Portions of the city of East Helena can be regularly expected to be non-attainment for lead and frequently non-attainment for TSP unless significant changes in vehicular traffic and industrial activities occur or an effective State Implementation Plan (SIP) is employed.
2. The principal sources of TSP in the key areas of East Helena are: Road dust, fugitive ore concentrate and residue emissions, carbonaceous sources (combustion and fugitive), ASARCO's zinc plant, and American Chemet's copper kiln.
3. The principal sources of Pb in the key areas of East Helena are: Road dust, fugitive ore concentrate and residue emissions, blast furnace upsets and ASARCO's zinc plant.
4. Road dust is among the major sources of ambient lead since it has been heavily contaminated near the ASARCO and American Chemet plants by fallout, track-out, spillage, etc. Any control strategy which is developed should deal with mitigating this problem as well as the control of direct aerosol emissions.
5. The data compiled in this study, combined with data from previous studies, meteorological records and the routine air pollution monitoring of East Helena and adjacent areas by the State of Montana and ASARCO has produced an extensive body of information. Correlation and comparison (including statistical multivariant techniques) between detailed plant operation records, meteorological records, ambient SO₂ levels, and chemical, elemental and mass data for individual 24 hour aerosol samples could produce additional insight into the relationships between sources and ambient concentration levels and is a recommendation for future work.

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